THE EFFECTS OF BEATING ON FIBROUS CELLULOSE

T H E S I S

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by

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P R E F A C E.

The experimental work described in the present thesis was carried out by the author when time and opportunity permitted in the chemical laboratory of Messrs. Tullis, Russell & Co., Ltd., Papermakers, Markinch, Scotland. The author wishes to express his best thanks and acknowledgments to the Head of the firm, Dr. Russell, for permission to undertake the work, and still more for the kindly interest and encouragement with which he has followed its progress. The industrial chemist is necessarily mainly concerned with matters of immediate practical importance. It will therefore be readily understood how the present experimental work is somewhat patchy and disconnected, and how it is spread out over a number of years. In many cases it could not be considered justifiable to procure the necessary apparatus and refinements to pursue a particular line of thought to its logical end. Another difficulty confronts the research worker in an industrial laboratory. He tends to get out of touch with the academic trend of thought, especially on pure scientific matters. The author regrets to some extent that he was only enabled to thoroughly remedy this condition at the close of his experimental work. Acknowledgment must also be made here of the assistance derived from the standardised beating and sheet-making methods and appliances devised by Dr. Macdonald and certain members of his staff. No

discussion of the beating effect would be of any value which did not appeal in the last resort to the strength qualities of the beaten sheet, and it was bound to be a considerable advantage to investigate such a problem in a laboratory and mill where standard methods of sheet preparation and testing had been in regular operation. Of the other chief methods of investigating the beating effect the flow-meter is an adaptation by the author of existing drainage testers, and the cohesion method has been devised to measure directly what is probably the central phenomenon in the beating process. Shrinkage of the paper sheet on drying is a well-known fact of papermaking. The author can only lay claim to have standardised its measurement, and to have considerably broadened the application of the method.

The author has not as yet published any of the experimental work described in this thesis. It appeared desirable to wait until the experimental facts could be fitted into a consistent theory of the physico-chemical nature of beating. Circumstances have arisen, however, which have necessitated a break in the work at a certain stage, and it is hoped that this is a suitable standpoint from which to review the whole group of phenomena involved in the papermaker's beating operation.

The references throughout the text to the experimental work and views of other scientific writers are necessarily very numerous in the case of a problem of this nature. In order to facilitate reference to such papers, and especially to the less important, which often do not call for careful study in the original, an index of references is included here. This embraces a list

of the quoted references which are abstracted in the B Abstracts of the British Bureau of Chemical Abstracts, and also such as have been abstracted by the Technical Section of the British Papermakers' Association in their Abstracting Service. The lists are as complete as the author could make them. A short key to the abbreviations used in the titles of the several less known technical journals is also included.

INDEX TO REFERENCES.

The following references, numbered as they appear in the reference lists at the end of each part of the paper, can be found in the B Abstracts published by the British Bureau of Chemical Abstracts. The year and page number of the B Abstract are given opposite the reference number in this thesis.

No.			No.		
9	Irvine	745 (1922)	45	Herzog	349 (1925)
	Heuser	688 (1921)	46	Herzog, Gonell	6 (1925)
12	Hess	9 (1922)	47	Curran	340 (1931)
15	Heuser	912 (1925)	50	Birtwell	606 (1930)
30	Hess	1022 (1930)	51	Kalb	153 (1928)
31	Ambronn	495 (1925)	52	Waentig	592 (1929)
32	Hess	812 (1930)	53	Kita	758 (1930)
34	Herzog	355 (1926)	54	Schwalbe	373 (1924) 937 (1924) 648 (1927)
38	Weimarn	186, 850 (1928)			
40	Lüdtke	455 (1930)	55	Olsen	96 (1930)
43	Nakano Not all Abstracted	937 (1929)	56	Nakano 552, Kienzl	608 (1930) 335 (1930)
			57	Minor	175 (1921)

No.				No.			
58	Wiscilenus	372	(1924)		Hawley	412	(1930)
59	Karrer	1145	(1930)		Meunier	1103	)1930)
61	Schwalbe	585	(1925)	88	**Baly**	744	(1931)
		876	(1925)				
		372	(1924)	98	Kanamaru	532	(1931)
62	Tingle	289	(1922)	99	Nakano See also ref. 76		
63	Kanamaru	12	(1929)	103	Oguri	1005	(1931)
						898	(1930)
64	Rochier	91	(1929)	109	Nakano	813	(1930)
66	Kullgren	984	(1930)	110	Weimarn	842	(1921)
		670	(1931)			440,626	(1925)
	Oeman	313	(1926)			186,850	(1928)
	Masters	977	(1922)		Herzog	254	(1921)
68	Schleicher	553	(1924)	114	Shorter	628	(1924)
	Schultze	852	(1928)	118	Nakano	91	(1929)
73	Jacobson	1009	(1924)	123	Lettermoser	1109	(1931)
74	Jupeau	873	(1929)	125	Neville	340	(1930)
						453	(1931)
75	Skark	9,583	(1922)	131	Rieth	1042	(1929)
76	Nakano	235	(1930)	135	Grund	655	(1930)
77	Davis	660	(1926)	138	Nakano	608	(1930)
		247	(1927)				
87	Meunier	276	(1927)	141	King	186	(1926)
	Denham	933	(1927)		Yoshida	177	(1932)
				147	Lecompte	255	(1932)

The following occur in the Technical Abstracts of the Technical Section of the British Papermakers' Association:-

No.4	Eberhardt	(1921)	No. 60	Liesegang	May (1927)
40	Lüdtke	April (1930)	68	Schultze	May (1927)
41	Trogus	May (1927)	112	Katz	Sept (1930)
	Nos.2,3,4	(1929)			
54	Schwalbe	(1921)	129	McGregor	Aug (1931)
	Also July, Sept	(1924)	135	Doughty	Aug (1931)
58	Wiscilenus, July	(1924)	137	------No. 10	(1929)

Abbreviations of Titles of Journals.

W.B. Wochenblatt für Papierfabrikation.

L.Ann. Liebig's Annalen.

P.F. Papierfabrikant.

C.Z. Chemisches Zentralblatt.

Z.P. Zellstoff und Papier.

Also Jahresbericht des Vereins der Zellstoff und Papier Chemiker und Ingenieure.

J.C.I.Tok. Journal of the Cellulose Institute of Tokyo.

J.S.C.I.Jap. Journal of the Society of Chemical Industry of Japan.

Proc.T.A.P.P.I. Proceedings of the American Technical Association of the Pulp and Paper Industry.

C O N T E N T S.

I

INTRODUCTION; PRACTICAL NATURE OF THE PROBLEM.

1. The experimental work and discussion which comprise this thesis are an attempt to throw some additional light on what is probably the central operation in the manufacture of paper, as distinct from that of pulp or half-stuff of various kinds. The operation of beating the paper pulp is at first sight purely a mechanical action, partly of size reduction and partly of separation of unit fibres which are already distinct, though loosely aggregated into fibre bundles. The aim of the process is twofold, (a) To get the fibre into such a state of free suspension in water, that it can be made into a coherent felted sheet on the modern paper machine, with existing appliances, and so as to get the necessary rate of output of finished product: (b) To help to impart certain desirable physical qualities to the finished paper,

(i) Appearance and texture - surface or finish, transparency, air and liquid porosity, bulk:

(ii) Mechanical qualities - handle, strength, stretch.

It will be clear that the above classification is somewhat arbitrary, that the two aims are interdependent, and that some of the desirable physical qualities are by no means wholly (or even mainly in every case) dependent on the results of the beating operation.

2. It must also be at once obvious that there is a

wide margin of choice as regards the initial fibrous raw material, and that very different physical qualities are called for in different types of paper. In the manufacture of newsprint for instance, the beating operation is hardly required, for blotting papers only a short and sharp cutting action is called for, whilst more and more beating effect is necessary to produce high class rag papers such as banks or loans. As regards papers where the beating effect is considerable, there is again a very marked contrast between a glassine tracing paper - transparent and to all appearance structureless - and an untearable manila paper. In the first the beating has been drastic, with the production of much fibre debris, and with great reduction in fibre length. In the second the beating has been long continued and severe, but carefully graded so as to preserve maximum length of fibre. It is quite obvious how such specialised results are dependent on the physical and microscopical characteristics of the various fibres, as is well shown in a paper by Strachan.(1) Such special cases, however, enable a general classification of the results to be drawn up somewhat as follows:-

(i) Separation of individual fibres from fibre bundles.

(ii) Cutting the fibres into shorter lengths.

(iii) Splitting the fibres lengthwise into fibrillae which are sometimes split off altogether.

(iv) Removal of entrained air from within the fibres.

(v) Production of fibre debris and structureless slime or mucilage.

(vi) Softening the fibres.

(vii) An undefined effect, loosely named 'wetness' or 'hydration.'

3. The question of economy in the beating operation resolves itself into three distinct problems.

(a) The selection of the fibres which are best adapted to impart the desired characteristics to the finished sheet and, where there is a choice, the selection of the most suitable mechanical appliances and conditions of operation to achieve the effect.

(b) The development of standards of measurement of degree of beating. As regards ultimate length of beaten fibres and degree of fibrillation such measurements must be made with the microscope, and are in general unsuitable for the control of manufacturing operations. The technique has been applied by Clayton Beadle in a study of the beating of various fibres, many years ago. I have heard of one mill at least where an attempt has been made, by means of a projecting lantern, to adapt the technique to manufacturing operations. It is otherwise as regards the somewhat undefined quality of 'wetness' or 'hydration.' Usually the 'feel of the stuff' in the beater and its behaviour on the papermachine wire are the only guide, although drainage testers are also in frequent use.(2) None of these are quite satisfactory, however, as they measure degree of dispersion rather than hydration. They do not help to elucidate the underlying phenomena.

(c) The reduction of power consumption during the beating operation. In the manufacture of fine papers

in particular the power cost of beating is a large item. It is not easy to give accurate figures, especially owing to the fact that in a paper mill power requirements and heating steam requirements go hand in hand, and in some cases the power may be largely acquired as a by-product. This will be the case if the power is derived from non-condensing engines or turbines, which also supply the steam for heating and drying. In order to give an idea of the approximate power requirements of beating in different cases, as compared to the total steam requirements, the following figures have been culled from several articles(3) in the Proceedings of the Technical Section of the British Papermakers Association. The underlying assumptions, believed to correspond to good engineering practice, are -

1 lb coal will generate 8 lbs steam at 200lbs/square inch pressure.

20 lbs steam in a modern non-condensing steam engine will yield 1 Horse Power Hour.

For all the quoted papers 10 cwts coal per ton of paper is deemed adequate for running the paper machine and drying the paper.

	Cwts coal	Lbs steam	H.P.H.	Beating H.P.H.
Operating machine in all cases	10	9000	450	------
Auxiliary power for news-print	10	9000	450	200
" " " cheap wood printings	18	16000	800	500
" " "all-Esparto paper	30	27000	1350	------
" " " all-rag fine papers, e.g. tissues	68	61000	3050	2200

In no case is any allowance made for the manufacture of pulp or half-stuff. The last column is from another source.(4)

It is at once obvious that there is an enormous field for economy. In the case of rag papers, however, where the principal operation is one of fibrillation, it is of course less likely that a better knowledge of the physico-chemical aspect of cellulose hydration will effect considerable economies. There the question is more of mechanics and engineering.

4. The mechanical aspect of beating will not be dealt with in this thesis. The papermaker's beater and refiner are adequately described in the practical text-books of the industry. The beater is designed to give an effect of cutting, shearing strain, and alternating pressures, carefully graduated in severity, upon the fibres when the latter are in aqueous suspension. The effect is usually produced between a set of fixed and a set of revolving metal bars, and of course there is usually a considerable loss of power in friction. The whole mechanical problem of beating has been very fully treated in recent years by Dr. Sigurd Smith in his comprehensive book, 'The Action of the Beater'.(5) By an analysis of the performance of the modern beater Dr. Smith estimates that in the case of rag fibres 50%, and in the case of chemical wood pulp 67% of the power is lost in friction and circulation.(6) His application of mathematical theory gives an adequate analysis of the cutting effect. When it comes to the 'wet beating' effect his conclusions are less satisfactory. In fact there is no satisfactory theory of the 'wet beating' effect, and there have been many attempts to evaluate it on mechanical principles, all quite arbitrary and empirical.(7)

5. A number of very interesting practical problems of papermaking, which really centre on the beating operation, will be referred to in the present thesis. Very conflicting opinions have been expressed on most of these topics in practical papermaking circles. A selection of the problems is given here.

(i) What change takes place in beaten stuff on prolonged steeping in water?

(ii) What are the effects of considerable rise of temperature during the beating operation and again when running the pulp over the papermachine?

(iii) How far is beating responsible for shrinkage and cockling of the finished sheet, and for subsequent shrinkage and expansion with change of atmospheric humidity?

(iv) How far are such papermachine devices as the shake on the wire, the suction boxes, and the presses responsible for the strength qualities of the finished sheet apart from beating?

6. Sufficient has been written to show the great practical importance of the beating operation, and the magnitude and diversity of the problems which it offers to the chemist and the physicist. It is quite obvious that the engineering problems cannot be solved on rational lines before the true nature of the change is understood, which fibrous cellulose undergoes during mechanical treatment in presence of water. Without that knowledge industrial practice and engineering developments must be at the best empirical, and may often be altogether on the wrong lines. It is clearly

necessary to pass under review the present state of the fundamental chemistry of cellulose and the recent advances in colloid chemistry, both in regard to cellulose derivatives and to colloids which are capable of affording analogies to the known properties of cellulose fibres.

The greatest difficulty at first is to devise suitable methods of measurement in order to disentangle the different effects which occur in the beating operation. It has been found to be almost impossible to measure truly simplex properties of the beaten pulp or to separate the coexistent mechanical and physico-chemical changes. One main object of the investigation has been to devise a practical means for rapid measurement of the 'wet beating' effect, a means which might be useful in industrial operations, either alone or in association with the drainage tester and the microscope. It is believed that appreciable progress has been made in this direction.

REFERENCES.

(1) J. Strachan, Tech. Sec. Proc. P.M.A. 6. 128.(1925)

(2) E.g. Schopper-Riegler & Green beating or freeness testers. See also Tech. Sec. Proc. P.M.A. 10.4.(1929)

(3) W. Adamson, Tech. Sec. Proc. P.M.A. 1.77.(1921)
A.B. Mallinson, Tech. Sec. Proc. P.M.A. 2.28.(1921)

(4) T.D. Nuttall, Tech. Sec. Proc. P.M.A. 1.180.(1921)
See also Eberhardt, W.B. 3319, 3391.(1920)

Strachan Ref. 1. gives power data which are much lower than those of Nuttall. From practical experience I incline rather to Strachan's figures. There are of course such wide differences in practice and in the quality of finished papers that any data must be purely illustrative and approximate. The last German reference (Wochenblatt Pap. Fab.) is to a list of represen-

tative figures from German fine-paper mills.

(5) S. Smith, 'The Action of the Beater,' published P.M.A. London.

(6) S. Smith, Tech. Sec. Proc. P.M.A. 3.270.(1923)

(7) S. Milne, Tech. Sec. Proc. P.M.A. 8.147.(1927)

II

THE CONSTITUTION OF CELLULOSE.

1. In order to understand the phenomena which underlie the beating of cellulose in water, it is necessary to take into account the knowledge of its general chemical reactions, and especially the new knowledge which has been gathered in recent years and has found expression in recent constitutional formulae. The relative backwardness of our knowledge of the physico-chemical relationship of cellulose and water makes it quite unnecessary to enter deeply into the constitutional theory, or into the still disputed details. An outline survey is alone necessary, but this should probably include the chemical hydration phenomena of the artificial silk processes.

2. There have been striking developments in cellulose chemistry in the last ten years. The position ten years ago is dealt with very fully by Mr. C.F. Cross in 'Cellulose'.(8) His conclusions may be roughly summarised as follows:-

(i) Cellulose is a saturated compound, resistant to hydrolysis and non-reducing. It is inert to dilute alkalis even at high temperatures and to mild oxidants such as hypochlorites or permanganates in neutral solution. Dilute mineral acids will hydrolyse cellulose, especially on boiling. The ultimate product of this reaction is dextrose. Strong acids and acid oxidants such as chromic acid will resolve cellulose much more quickly and effectively.

(ii) Natural and artificial forms of cellulose contain

equilibrium amounts of hygroscopic moisture. This is related to the active hydroxyl groups of the molecule, as the amount is lessened after esterification. It is shown by absorption phenomena that the hydroxyl groups are of both basic and acid function. Chemical reactions of esterification and alkali- cellulose formation also show this. It is possible to peptise cellulose in water by suitable solvents. In all cases, e.g. $ZnCl_2$, there is a simultaneous attachment to both basic and acid groups. The solution of cellulose is always, to some extent, connected with the depolymerisation of a percentage of the molecules, and the physical properties of the regenerated cellulose are the more valuable in so far as the degradation has been less. It is concluded that the hydroxyl groups in cellulose are in a state of mutual suppression. Cellulose is known to be an endothermic compound. The viscose and cuprammonium solvent actions are similar. It is to be observed that in all cases the regenerated cellulose has a greater hygroscopic moisture than the original cellulose, and that its hydroxyl groups undergo esterification more readily than before.

(iii) Several cellulose esters are known, but the nitrates and acetates are the only ones of technical importance. It is generally necessary, espedially in the case of the acetates, to accelerate esterification by the action of catalysts. The final acetate originally discovered was chloroform-soluble, but insoluble in acetone. A controlled partial hydrolysis has given the modern product, which is acetone-soluble. The

saponification of the cellulose esters is fairly easy to accomplish. It is very unlikely that any of the cellulose esters form true solutions in any solvent: peptisation is a better word. The question as to how many separate nitric and acetic esters exist is still in dispute. X-ray measurements of recent years have made it probable that only the tri-esters on the $(C_6H_{10}O_5)$ formula exist.

(iv) There are of course many different natural forms of cellulose. They are graded by Mr. Cross according to (a) resistance to hydrolysis and oxidation, (b) regeneration yield from cellulose solvents, (c) esterification yield. American 'Sea Island' cotton purified by a very mild treatment is chosen as a standard by Mr. Cross. In the present investigation a purified, bleached sulphite wood cellulose will be used. Compared to cotton, sulphite wood cellulose is slightly more reactive. Its higher 'copper number' indicates a higher proportion of active CO groups. The difference is, however, comparatively slight.

3. Knowledge of the structure of cellulose has been largely based upon the knowledge of its hydrolysis products, and of their constitution. It was known a good many years ago that some dextrose could be obtained by the acid hydrolysis of cellulose. J.C. Irvine and E.L. Hirst[9] by using the method of controlled acetolysis, with sulphuryl chloride as a catalyst, were able to isolate a crystalline glucose derivative corresponding to a yield of 95% on cotton cellulose. A great many other investigators have been occupied with the problem,

but most were contented without isolating crystalline end products corresponding to the full yield. Remembering the labile nature of the monoses in solution, and the striking differences between the different complex polysaccharides, the difficulties of constitutional research and the need for clear-cut precision of method will be evident. An account of the newer views of the structure of glucose will be found in the recent book by W.N. Haworth, 'The Constitution of Sugars.'(10) It is sufficient to point out here that β-d-glucose, which is the sole hydrolytic product of cellulose, has a 'pyranoid' constitution, i.e., it involves a 6 atom ring of 1 oxygen and 5 carbon atoms. Haworth prefers a 'strainless' ring with the atoms arranged with their centres on two parallel planes. This arrangement permits the linkage of glucose residues to form more complex polysaccharides, and will be referred to later in connection with the spiral structure of the cellulose micelle. The glucose structure has been confirmed by X-ray methods. Cellulose and starch differ from each other in their hydrolysis products which are β-d-glucose and α-d-glucose respectively. Thus cellulose is a β-glucose β-glucoside complex.

It is also possible to obtain by the controlled hydrolysis of cellulose more complex carbohydrates such as cellobiose. The composition of cellobiose is dealt with by Haworth in the book already cited. Cellobiose contains two glucose residues linked at the 1 and 4 carbon atoms respectively by an oxygen bridge. Two controversies have raged over the cellobiose resolution

of cellulose. The first deals with the yield of cellobiose obtainable, and the second as to whether cellobiose is really an integral part of the cellulose molecule. In a paper on the constitution of cellulose Hibbert[11] deals with this question, and with the whole constitutional position as it was in 1921. About the same time Hess[12] deals with the question, and the latest views on the possible yield of cellobiose, placing it at 60%, are given by Meyer and Mark[13] in a paper which will be referred to again. The second controversy is interestingly dealt with by Freudenberg[14] in a recent paper on the constitution of the polysaccharides. He recalls that Willstätter and Zechmeister have gone further and have isolated crystalline cellotriose and even a tetraose by the arrested hydrolysis of cellulose.

4. Before proceeding to the chemical evidence as to the linkage of the glucose residues in the cellulose molecule some results of the application of physical methods to the problem of the size of the cellulose molecule will be briefly discussed. (a) Cryoscopic. E. Heuser[15] has made determinations of molecular weight on the methyl celluloses in water, and obtains figures like 6-8000 for cotton wool, and only 900 for cellulose dextrin. The molecular weights are not stable and they tend to diminish with time. The results are claimed as evidence of the polymerisation of the cellulose substance. Determinations in complete absence of air have been made on trimethyl-cellulose by Hess and Weltzien[16] Freudenberg is very critical of all results obtained by the cryoscopic method. In fact he rejects them outright as liable to a

number of errors, one of the main ones being the 'retardation of refreezing' which seems to occur with such solutions.

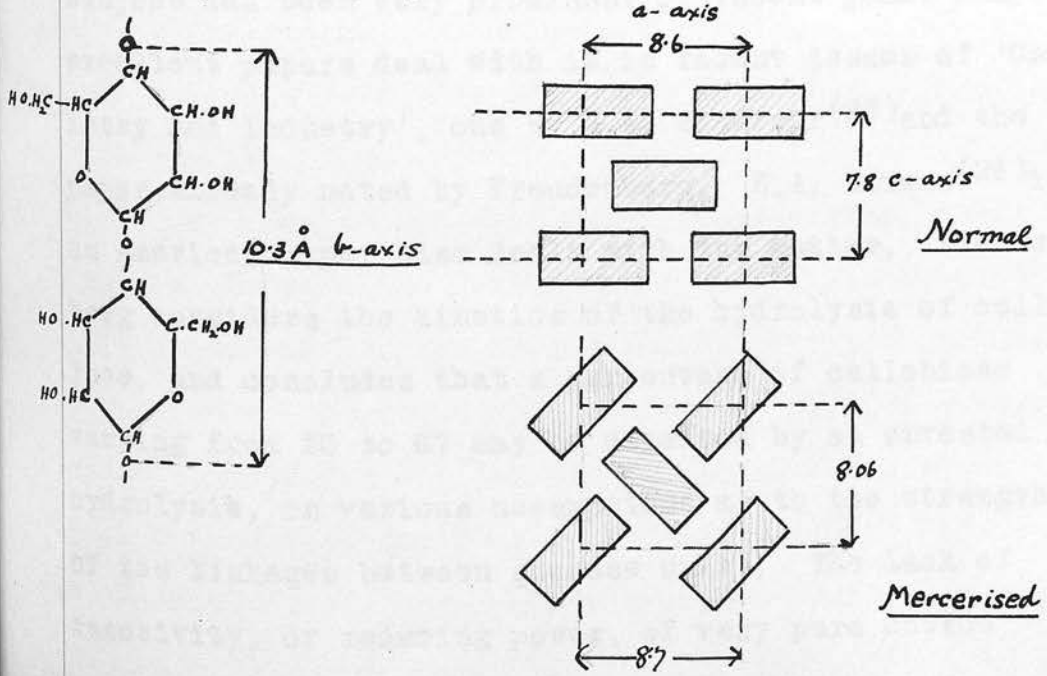
(b) Diffusion method. Herzog and Krüger[17] estimate the size of cellulose acetate particles at 5$\mu\mu$ in ethylacetate and 35$\mu\mu$ in epichlorhydrin. Krüger[18] in another paper uses the nitrates and finds values for the dimensions of the crystallites (14$\mu\mu$ sulphate pulp, 22$\mu\mu$ sulphite pulp and 34$\mu\mu$ cotton). In the viscose process he finds that 'ripening' causes orientation and agglomeration from 14$\mu\mu$ to 24$\mu\mu$. He assumes 10$\mu\mu$ for the dimension of the cellulose molecule. It appears[14] that the diffusion method is not altogether reliable either. A further estimate has been obtained recently by Katz and Samwel[19] by estimating the thickness of a unimolecular cellulose layer, by a physical method.

(c) It is not too much to say that the key to the ultimate structure of the cellulose molecule has been given by the new technique of X-ray analysis. The fundamental principles of the method have been firmly established and are well described in the 'Introduction to Crystal Analysis' by Sir W. Bragg.[20] The application of the method to cellulose fibres and a description of recent results are given by G.L. Clark[21] in a recent American paper. The literature on the X-ray analysis of cellulose is fairly extensive. It is enough to point out that earlier investigators favoured a rhombic crystalline structure. Herzog[22] took this view as far back as 1920, and he also assumed a building unit of $(C_6H_{10}O_5)_4$ magnitude. A comparison is given of the merits of the

open chain, the closed ring, and the internal anhydride structures. Viscose and acetate silks were also examined, and the latter declared amorphous. The two classical investigations on the subject are, however, those by Sponsler and Dore[23], and by Meyer and Mark.[13] The latter paper claims that cellobiose is preexistent in cellulose, and that the cellulose space lattice unit is built up of 4 glucose residues. There is an exhaustive survey of the applicability of different crystalline forms to the X-ray data, and a monoclinic unit crystallite is finally selected as most probable, with axes of lengths (Angstrom units)

a = 8.65 - 8.75
b = 10.25 -10.35
c = 7.8 - 7.9

The b axis in the accompanying diagram is in the length direction of the completed fibre and corresponds to two glucose units in length. It is shown how the diagram can be adapted to illustrate the opening out of the structure during the swelling of cellulose in mercerisation phenomena, when the dimensions become a = 8.93, b = 10.00, c = 8.06.



Meyer and Mark suggest the union of about 40 glucose residues in the b axis, or the fibre direction in a helically arranged chain. The union is by β-glucosidal links in the 1.4 positions of the pyrane rings. From 40 to 60 such chains lie side by side in the a and c directions, and are linked by secondary valencies, or micellar forces. The result is the cellulose unit or micelle.

(d) The use of the physical 'optical rotation' method has been fundamental in the study of the hydrolysis products of cellulose. Hess[24] has applied it to the cuprammonium solutions of various celluloses, and he uses his results to demonstrate the essential identity of celluloses from different sources, and as an argument in favour of a $C_6H_{10}O_5$ and not a $C_{12}H_{20}O_{10}$ unit.

5. The mode of linkage of glucose residues in cellulose has been already discussed in connection with the views of Meyer and Mark. At the present day the conclusions of Meyer and Mark are pretty generally accepted. The subject has been very prominent of recent years and two excellent papers deal with it in recent issues of 'Chemistry and Industry', one by A.W. Schorger[25] and the paper already noted by Freudenberg. E.A. Hauser[26] in an American paper also deals with the matter. Freudenberg considers the kinetics of the hydrolysis of cellulose, and concludes that a percentage of cellobiose varying from 30 to 67 may be expected by an arrested hydrolysis, on various assumptions as to the strengths of the linkages between glucose units. The lack of reactivity, or reducing power, of very pure cotton

cellulose has been rather difficult to explain with straight chain linkages. Loop formation in the chain has been postulated to account for this. There is probably agreement however, that within the micelle length linkages are due to primary, and breadth to secondary valencies. It seems probable that there is still a residual affinity available to bind the micelles, and that this residual affinity is again vectorially differentiated as regards the micellar axis. Schorger gives some very interesting views on this topic. Many controversial issues remain, but it is not possible to pursue the topic further in this thesis, and it is sufficient to note that there are reasons for differentiating between the length and breadth, and also between the strengths of the longitudinal and transverse binding linkages in cellulose units. There is also good reason for believing that the molecule is to a certain extent loosely built transversely, and that it is possible for groups to enter the micelle, during swelling with water or other reagents, without severing the transverse linkages. The general stability and inertness of the cellulose molecule is discussed by Freudenberg in comparison with starch.

6. A few remarks are necessary on the physico-chemical changes of cellulose during the artificial silk processes. This is mainly because of the peptisation and swelling phenomena which occur. The two papers by A.W. Schorger and E.A. Hauser are of interest, and also two recent papers by C.J.J. Fox[27] and H. Levinstein.[28] From a consideration of these papers a pretty complete outline

of the reactions of cellulose both for viscose and acetate silk manufacture may be obtained. The first point of interest is the X-ray structure of the cellulose. A profound modification of the diagram takes place during conversion to alkali cellulose, and also with swelling in cuprammonium solution, as was found by J.R. Katz and H. Mark.[29] The change is not entirely reversible. There are many papers on the subject of the X-ray diagrams of the artificial silks. Generally viscose silk is held to be crystalline; Meyer and Mark[13] claim that cellulose nitrate is crystalline; for a long time acetate silk was believed to be quite amorphous, but Clark[21] claims that a clear-cut crystalline X-ray pattern has been obtained for cellulose acetate; probably ethyl cellulose is still believed to be amorphous. Schorger[25] says that the $(C_6H_{10}O_5)$ unit has 3 hydroxyl groups in the 2, 3, 6 positions, one primary and the others secondary, and that beyond this point 'there is almost total darkness' as far as our structural knowledge is concerned. The X-ray diagrams, however, show that the cellulose micelle has been altered during esterification, and the presumed amorphous nature of the acetate was held to show that the acetyl groups were so large as to disrupt the orderly spacing of the micelle. The subject will be again referred to in connection with evidences of hydration and fibre structure. Meanwhile the evidence from X-ray analysis is strongly in favour of the existence, as separate compounds, of the triesters alone. Other esters give mixed diagrams of triester and unchanged cellulose.

The conditions which are essential to swelling and peptisation are of interest. It seems to be agreed that a mild and very partial hydrolysis or oxidation is a prerequisite. Even then solution does not always follow swelling. Swelling alone occurs with aqueous NaOH solu. $>18\%$ and again, even if CS_2 be added, only swelling occurs if the alkali is too dilute. The conditions essential to peptisation according to colloidal theory must be present, as well as the necessary protective colloid or peptising agent, formed by chemical action on the cellulose molecule. The presence and functioning of both basic and acidic hydroxyl groups in the cellulose seems to be essential for solution to occur. The viscosity of the resulting solution seems to be dependent on two factors, (i) the size of the micelles, or the degree of physical degradation of the cellulose, (ii) the changes in micelle envelope water due to osmotic action. This is especially the case during the storage of viscose solutions.

The tensile properties of regenerated celluloses are of interest. All cellulose materials, natural and artificial, are characterised by a certain degree of orientation which manifests itself in mechanical strength properties. All the artificial silk processes are degrading from this point of view, and the products have a lesser degree of orientation than the original natural cellulose. A higher degree of orientation seems to be attained in Lilienfeld silk by the simple expedient of spinning a less degraded solution into a stronger acid bath. The question of physical degradation and

disorientation of cellulose will be met with in considering 'beating' for papermaking. A discussion of the degree of orientation of different cellulose materials by the X-ray method is given by Hess and Trogus.(30)

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III.

THE MINUTE STRUCTURE OF NATURAL CELLULOSE FIBRES.

A good deal of recent work on the minute structure of the natural cellulose fibres has a very important bearing on the phenomena of the beating process. Such considerations are conveniently dealt with under three headings, the first describing evidence of a microscopic nature in favour of the organised crystalline structure of fibres, and a few allied topics, the second on the recent discovery in natural fibres of a non-cellulosic membrane system, and the last on the evidence from X-ray analysis of the successive building units of fibres, and on the evidence for or against substantial changes in the ultimate micelles as a result of beating.

1. Microstructure. H. Ambronn[31] in an interesting paper has found microscopic lines of cleavage in certain long bast cells, the angle of inclination to the fibre being fairly constant. They are also seen in ribbon-like fibres, although they are harder to detect in cotton owing to the helical twist of the fibrillae. Ambronn suggests that the action of dyes and chemicals will be more intense along these lines, and finds a strong similarity to the cleavage planes of crystals. The existence of slippage planes in cellulose esters is also presumed by K. Hess.[32] Thus considerable complexity of structure is to be found even in artificial silks produced under very uniform conditions, and J.M. Preston[33] finds a skin effect on

viscose rayon which, on the dyed yarn, gives rise to double refracting properties.

Many investigators see the necessity for admitting the existence of some form of colloidal inter-fibrous cement. R.O. Herzog[34] calls the fibre a two-phase system and allocates many of the fibre properties, such as elasticity and hygroscopicity, to the cement. He uses the analogy of crystal slippage planes in metal working in order to explain the elastic properties, and shows that the strength of the fibre does not diminish at very low temperatures (liquid air), but the stretch does. It is concluded that, as the strength of natural vegetable fibres is not increased by tension, as in the case of artificial fibres, the cement and fibre substance must be very well proportioned and distributed in the natural fibre. The existence of the colloidal cement is also admitted by H. Mark.[35] An interesting comparison of the strengths of artificial and natural fibres is given by Herzog in the paper already cited, although the new Lilienfeld silk gives a more favourable comparison.

Besides the interesting paper previously mentioned on the physical characteristics of the papermaking fibres, J. Strachan[36] has outlined his views on the fibrillar structure and thinks the known double refraction property of cellulose fibres is not a result of strain during growth, but simply owing to the crossing at a constant angle of several layers of thin rods superposed on each other. The double refraction of diatomaceous silica is instanced as a comparison.

Not very much has been learned from the break up of the visible fibre, but G.J. Ritter[37] has succeeded in decomposing it so as to leave very minute fusiform bodies, which are just within the limits of microscopic visibility. For this purpose the graded hydrolysing action of 68 - 77% H_3PO_4 was used on delignified spruce and elm fibres. The fusiform bodies are claimed to be the building units of the fibrils. The existence of a colloidal cement is also presumed.

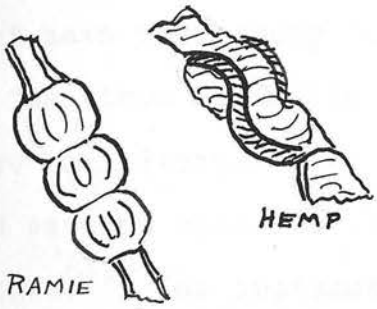
The existence of fibrous structures is not confined to organic nature. P.P. von Weimarn[38] has noted the development of thread-like bodies in soap solutions. He has generalised the phenomenon, and has shown that double decompositions accompanied by the rapid formation of precipitates in concentrated solutions may lead to the formation of thread-like structures. The growth or disappearance of the threads is seen to depend on the balance of osmotic pressures within and external to the fibrous or tube-like precipitate. The theory is of great interest, as natural cellulose fibres have very probably been formed by a coagulation process from a liquid, and it is unlikely in consequence that the natural fibres should be perfectly homogeneous in their resistance to hydration or dispersion. Further evidence as regards the optical anisotropy of inorganic crystals of the regular system is offered by Ambronn[39] in the case of gold and silver crystals formed in narrow spaces.

3. The natural cellulose membrane system. A contribution of considerable importance concerning the micro-

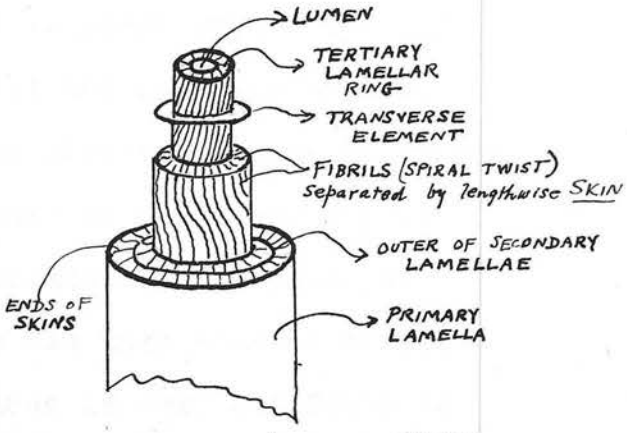
structure of natural cellulose fibres, and one which may go some way towards explaining the phenomena of beating, was made by Max Lüdtke in several recent papers.[40] This is referred to by K. Hess[32] in the paper already quoted. A review of modern views on swelling and structure of cellulose fibres, accompanied by an interesting discussion, is also given by C. Trogus.[41] The matter has aroused considerable interest, and has been taken up by other investigators.

The views of Lüdtke are best illustrated by the accompanying sketch. His first work was done on bamboo fibre, but the results have been considerably extended. The centre of the fibre is occupied by the lumen surrounded by the tertiary lamella. Outside this is the secondary or cellulose lamella arranged in layers, and divided by concentric cylinders of skin substance. The outer or primary lamella is also radially divided by fine, almost imperceptible lines attributed to the presence of thin skins, and the strips often give rise to a spiral appearance. These strips are built of fibrillae, which are the smallest microscopically visible units. There seem also to be present in the fibre transverse discs of a skin substance. It is probable that the skin substance, perhaps as well as the primary and tertiary lamella is furfuroidal in nature. Many plant fibres show the same arrangement when partially xanthated or treated with cuprammonium reagent, because by such a differential etching the more resistant membrane substance becomes prominent. The result produced by swelling agents on fibres is similar to the formation

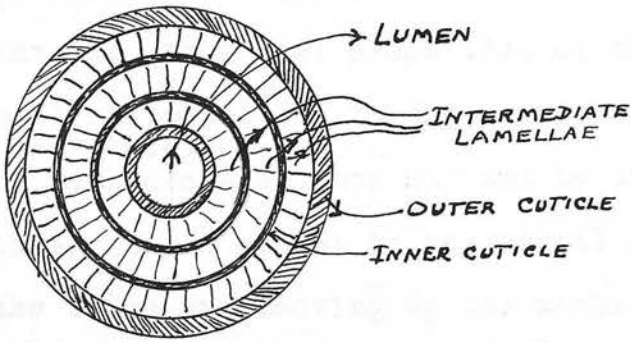
of a kind of bead necklace, and can be seen on beech, pine, wheat, cotton, sisal and bamboo fibres, particularly the latter. The bead necklace effect is in fact taken to be the visible sign of the existence of a membrane system in the fibre.



BEAD NECKLACE EFFECT



LÜDTKE FIBRE STRUCTURE



NAKANO FIBRE STRUCTURE

The foregoing may be taken as a fair summary of Lüdtke's views on cellular fibre structure. He goes on further to show how they can be applied to cellulose problems. The ripening of alkali cellulose may be a case of cracks developing along membrane lines, where chemical reactivity will be greater than usual. Swelling in water may occur where the membrane system has been damaged in the beater. There will be enhanced moisture absorption by the fibre debris and cellulose

mucilage of beaten stuff. The contraction on mercerisation is a consequence of the non-swelling transverse membranes (see illustration) and bead formation is also explained. An alteration of the X-ray diagram is also to be expected. Alterations in plant growth and nutriment have been shown to affect the membrane system.

The views of Lüdtke on the membrane system in fibres have been discussed by a number of cellulose experts, and several opinions are available in the paper of Trogus.[41] For instance Hess has been able to explain why fibrous trimethyl cellulose is very difficult to disperse in water, but becomes readily dispersible if precipitated from neutral solvents. Hess also points out elsewhere that the mechanical properties of the fibre may be largely attributable to the membrane system, and that the membrane substance may not be the same for all fibres. There appear to be several methods of etching the fibre and showing up the membrane. Trogus says that Hess partially acetylated the fibres in one method, and that in another he steeped cotton in an atmosphere of HCl gas and then removed the hydrocellulose with 2N NaOH solution.

The description of Lüdtke's membrane theory would be incomplete without a few words on the probable nature and amount of the membrane substance. Trogus thinks that the substance must be a polymerised glycuronic acid or anhydride, from the strong reddish-violet colour obtained from a lignin-free fibre by the action of a solution of phloroglucin in absolute alcohol acidified with HCl. At one point he estimates

that the amount of membrane substance required may be as little as 0.2% to 0.5% of the fibre substance. It is to be noted that Schwalbe u. Feldtmann[42] found d- glycuronic acid in bleached straw pulp.

The membrane system of cellulose fibres has also been investigated by Japanese workers,[43] who give a number of micro-photographs showing the bead necklace effect and the spiral structure of different fibres. The matter is somewhat polemical, Sisido and Nakano not being entirely in agreement with each other or with Lüdtke. On a previous page Nakano's diagrammatic section of a typical fibre is given. Nakano is disinclined to believe that the whole of the cellulose lamella has the Lüdtke structure, or that the transverse membranes exist. However, Lüdtke's main ideas seem to be established and confirmed for a good many other fibres.

Nakano has also demonstrated a series of planes perpendicular to the fibre axis which he thinks are planes of mechanical weakness, and which may be due to intervals of growth. W.L. Balls[44] has identified longitudinal growth rings in the fibre, which he thinks correspond to alternations of daily growth. On the whole it is hardly to be expected that fibrous cellulose will exhibit complete homogeneity in its physical and chemical behaviour.

3. X-ray evidence as to fibre structure. The method of X-ray analysis is a very valuable means of detecting alterations in the structure of the ultimate fibre units. The method is limited, however, to detecting differences which cause disorientation of a sufficiently large

proportion of what are called the ultimate micelles. The micelle as a unit of structure is the conception of the botanist Von Nägeli, and it has now been extended to inorganic substances as well. The new conception of cellulose fibres is somewhat as follows. The ultimate fibre may be taken to be what is separated in the papermaker's beater before cutting has taken place. At least this is a convenient conception. Its thickness may be roughly 20μ -30μ. Herzog[45] considers that there may be up to 100 fibrillae united to form the ultimate fibre. The number will vary widely with different types of fibre. The same author estimates that from 10 to 100 crystallites unite to form a fibrilla. The multiples given must be taken to refer to one dimension, although it is evident that the ratios will differ widely as regards length and breadth. Lastly Meyer and Mark[13] suggest that the space lattice cell is about 10Å X 8Å X 8Å, being composed of four glucose residues, and that the micelle is composed of chains of from 30 to 50 glucose units bunched together in groups of from 40 to 60 chains, each micelle containing about 2000 glucose units.

The micelle size may be therefore about 20$\mu\mu$X6$\mu\mu$. Trogus says 30 - 50$\mu\mu$X3 - 5$\mu\mu$. An average ultimate fibre may be 200 - 2000μX20 - 30μ. It seems certain that the long micellar form is a building plan which is used by nature in the construction of the successive units of fibrillae and ultimate fibres.

Complete parallelism of the micellar axes is not preserved however, and Herzog has shown that the micelles

are inclined to the fibre axis at a characteristic angle, giving a spiral structure in many cases. He finds no organised arrangements as regards the cementing substance. Trogus[41] gives the inclination to the fibre axis in a number of cases, viz. 2° for hemp, two sets of fibrillae for ramie inclined at 4° and 7° respectively, and an inclination of 45° for cotton.

Before considering what information the X-ray diagram can afford as regards beating, it is as well to consider the limits of the X-ray method. The kind of information available in this way, so far as cellulose fibres are concerned, is clearly described in the previously quoted paper by G.L. Clark[21] and in an earlier paper by Herzog and Gonell.[46] Perfectly orientated crystalline fibres can be made to yield a point diagram. Completely disorientated crystallites will give a ring diagram. Amorphous material will give a diffuse blur and no diffraction pattern at all. Natural celluloses in many cases give point diagrams, artificial fibres always give a mixed diagram with a partial orientation effect. If the crystallites are arranged in a parallel manner in the micelles, which in their turn are arranged in a sort of helical twist about the fibre axis, the diagram will show circular diffraction arcs with reinforced intensity near the points of the point diagram, and it is possible from measurements of the arcs to predict to some extent the angle of the spiral. It is presumed that usually the micelles are parallel in the fibril, which is twisted in the fibre itself. The twist of the fibrillae is actually rendered visible to some extent by

the etching methods used to demonstrate the membrane structures. By measurements of the intensities of the diffraction spectra and the breadth of diffraction bands various inferences can be drawn as to the size of the micelles. Changes which take place outside the micelles will not affect the X-ray diagram, except in so far as disorientation of micelles may accompany the change. It is clear also that small proportions of altered micelles are not likely to be detected by this method.

The X-ray method has given definite pronouncements on the changes which take place on mercerisation, parchmentisation by strong acids, and esterification. In these cases quite a different diagram is found, and on the reversal of the process the diagram often shows both the original and the altered states. Katz and Mark[29] have compared such changes with the action of concentrated solutions of neutral salts on cellulose. In the latter cases no change in X-ray diagram was found, even when the action of the neutral salt, e.g. $ZnCl_2$, was pushed to the point of extreme swelling just short of actual peptisation. Katz and Mark attribute the changes to an opening out of the micelles, and estimate that mercerising enlarges the space lattice by about 4% in the transverse direction. Apparently no similar deep-seated change occurs during peptisation with neutral salt solutions.

The effect of beating on the micellar structure has been investigated by several workers. Trogus[41] whilst holding that the swelling of fibres in water produces

a barely perceptible shortening along with a transverse expansion of from 20 - 30%, says that there is no change in the X-ray diagram of the fibre. A very slight change has been noticed by Curran, Simmonds and Chang,(47) and none at all by J.W. Rowe(48) after considerable beating treatment of the fibre. Trillat(49) treated cotton linters in a KEK colloid mill and found no change thereafter. If the proportion of the micelles affected was small however, the only effect would be a certain diffuseness in the diagram. Considering the intense swelling action of some of the neutral salt solutions used by Katz and Mark, it is hardly to be wondered at that even a severe beating treatment causes no change in the X-ray diagram. In the same way the viscosity of a cuprammonium solution of cellulose fibres prepared in a standard manner is an accepted criterion of the size and degree of integrity of the micelle, and is a more sensitive indicator of micellar degradation than the X-ray diagram. Rowe found that the viscosity in cuprammonium was also unaffected by previous beating treatment.

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IV.

CHEMICAL CHANGES DURING BEATING.

It has been found necessary to deal with several rather distinct topics in this section, in order to clear the way for the discussion of the physico-chemical aspects of the problem. It may be stated at once that it is in the last degree improbable, that a compound of cellulose and water in stoichiometric ratios can be shown to exist. The vapour pressure dehydration curves of moist ordinary and beaten celluloses will be discussed later, when considering swelling phenomena; it is enough to say here that the curves are quite continuous, and that all except a minute fraction of moisture can be removed from cellulose below 100°C. The chemical changes undergone by fibrous cellulose in pure water, or in very dilute aqueous solutions, are of two kinds, (a) the adsorption of the solute, (b) the partial degradation of the cellulose. The two groups of phenomena are inter-related.

1. As the chief 'chemical' theory of beating gives great prominence to the formation of degradation products of cellulose, something must be said about hydrocellulose and oxycellulose, and about the criteria of purity of cellulose. There is a great deal of literature about this. Cross describes the properties of hydro- and oxycellulose. The two products are not always easy to distinguish from each other. Generally they are characterised by increased affinity for water, solubility in alkaline solutions, increased affinity for certain basic dyestuffs and, most important of all, reducing power as evidenced

by increased copper number. Increased copper number and affinity for basic dyes do not always go hand in hand. Hibbert measures oxycellulose by the amount of CO_2 evolved on refluxing with standard hydrochloric acid. The measurement of the absorption of $Ba(OH)_2$ from solution is an extremely simple test for only slightly degraded cellulose. In future experimental work in this paper an α cellulose value and a standard copper number have been used. Hibbert[50] gives an excellent discussion of criteria of purity for cellulose. The application of such criteria to a study of beating is well shown in the previously quoted paper by Curran, Simmonds and Chang.[47] In the artificial silk industry a partial degradation of cellulose is desirable in order to aid peptisation. The lowering of the viscosity of the cuprammonium solution is then a very good measure of such degradation. It seems unlikely that oxycellulose is a definite compound. Kalb u. Falkenhausen[51] have shown that cellulose in cuprammonium solution can be oxidised in a continuous manner without any definite intermediate stages, until it is completely soluble in NaOH solution. Herzog[45] finds that X-ray analysis fails to distinguish between cellulose and hydrocellulose. Waentig[52] discusses the part played by the copper as an oxygen carrier to the cellulose, whereas Kita[53] claims to have shown that oxidation plays no part at all in the lowering of the viscosity of cuprammonium solution of cellulose.

2. C.G. Schwalbe[54] is the great protagonist of the chemical degradation theory of beating. He believes

that in the course of beating, cellulose degradation products are formed, and that these products, being highly hydrated, are readily absorbed by the unchanged fibres, with the result of catalysing the further degradation of the cellulose. A non-fibrous mucilage or slime is thus produced, which consists of a complex of fibre debris and cellulose dextrins, containing hydro- and oxycellulose. In order that the process may be rapid it is essential for the raw pulp to have a reasonably high copper number or reducing activity. Where this is not the case Schwalbe prescribes a pretreatment of the pulp with dilute acids or mild oxidants, and the process of subsequent beating is greatly accelerated. Schwalbe claims that the pretreatment is not only applicable to beating, but is also very useful when the pulp is to be used for artificial silk manufacture. Numerous patents have been taken out by Schwalbe[55] and others along these lines.

The practical papermaker is well aware that there is a sound basis of fact beneath the ideas of Schwalbe. It is well known that it is very difficult to get 'wet beating' with pure wood pulps of very high α cellulose content, and that the easiest pulps to wet are the 'slow-cooked Mitscherlich sulphites,' which have undergone a very mild purification treatment, and have a high copper number. As to the value of the acid pretreatment opinions are more varied. On the one hand there is always a certain buffer salt action in papermill waters, and on the other the papermaker is chary of risking the corrosive action of acids on bronze

beater bars. Nakano[56] has investigated the matter, and finds no benefit whatever from pretreatment with dilute acids, even with lactic acid which is specially recommended by Schwalbe. Nakano does find that copper number is increased by beating, but that the increase is not dependent on the original copper number, nor on the beating degree. It is therefore quite reasonable to admit that the formation of small amounts of degradation products plays a part in the phenomena of beating, but it seems unlikely that the principal change which occurs during beating is mainly ascribable to impurities in the cellulose. The further progress of the change is ascribed to a catalysis of the action by the mucilage itself. Minor[57] explains how important it is that the mucilage should be strongly adsorbed by the fibres. Wiscilenus u. Gierisch[58] have submitted filter papers to severe mechanical action for a period of 255 hours in the dry state, and have observed a partial solubility of the product in water to the extent of only 0.6%, along with an increased copper number. The main result in this case would appear to be great swellability in water, but the increase in chemical reactivity is also striking. A further indication of the influence of mechanical structure on reactivity as regards degradation is given by Karrer,[59] when dealing with the resistance of artificial celluloses to enzymes. It is certainly possible to imagine a modus operandi, whereby the cellulose dextrins will so lower the surface tension at the cellulose-water interface, as to promote conditions which favour swelling and further degradation.

From the scientific point of view it is eminently desirable, however, that the physical and colloidal aspects of the question should be studied by themselves if, as seems likely enough, pure celluloses show the essential phenomena of beating without suffering chemical degradation.* It should be added that a similar hypothesis of peptisation by degradation has been put forward by Herzfeld u. Klinger[60] for albumen, which they claim is only soluble in water because it is surrounded by a film of decomposition products. Again this view has been strongly opposed by others.

As a result of his investigations Schwalbe[61] proposed certain measures of the beating effect, viz:-

(a) Increased moisture adsorption in a saturated atmosphere, 25-30% for mucilage, 16-18% for fibres. He drops this idea later.

(b) Water retention of pulp after centrifuging in a standard manner. In this way a lactic acid treated pulp retains 500% water, and an untreated pulp only 150%.

(c) The adsorption of hydroxides from basic solutions of iron and aluminium salts. Ferric acetate is used for this, and the adsorption increases greatly as beating progresses. In a later communication Schwalbe admits ~~that~~ the influence of incrusting impurities on the adsorption.

3. The increased adsorption of basic hydroxides by beaten cellulose was designed by Schwalbe as a measure of the development of free acidic hydroxyl groups in the course of beating. Cross quotes figures for the

* See experimental work IX, 2.

adsorption of both sodium hydroxide and mineral acids from very dilute aqueous solutions by purified cotton cellulose. The existence of weak, partial, unsaturated valencies in pure cellulose seems to be beyond doubt. When it comes to the adsorption of cations from salt solutions the matter is more disputable, however. Tingle[62] examined the question carefully as far as aluminium salts were concerned, and pronounced a very qualified negative opinion. Kanamaru[63] has boldly ascribed the property to impurities in the shape of ash substances and degradation products. Rochier[64] is of the opinion that the adsorption takes place with pure cellulose, and that it is of the nature of a base exchange. Rochier's results have been thoroughly investigated and confirmed by S.R.H. Edge[65] in a recent paper. Kullgren[66] has also observed the base-exchange phenomena with other metallic salts. It is therefore probable that the base-exchange property in an aqueous solution is due to the cellulose itself, and not to any impurity. With impure celluloses, and when notable degradation occurs during the course of beating, the presence of degradation products of acid function will alter the character of the phenomena altogether, with the result that the adsorption of mordant salts may then be a good measure of degradation.

It is evident that if purified cellulose exhibits the base-exchange property, the fact may have important consequences in the phenomena of beating. It is desirable therefore to consider briefly the analogous case of the permutites and colloidal clays, which has been

carefully investigated by Wiegner[67] and his coworkers. Wiegner concludes that a permutite particle is a hydrated micelle consisting of an ultramicron of hydrated aluminium silicate, an inner surrounding layer of anions and an outer swarm of cations. Outside ions from the surrounding solution can enter the outer swarm by base-exchange, the exchange being very largely determined by the hydration values of the entering cations, although solubility and ionisation factors may assume a greater importance in some cases. The order of exchange preference is therefore that of the lyotrope series of Hofmeister. A suspension of clay particles may show an acid or alkaline suspension effect according to the circumstances, i.e. the clear filtrate and the suspension may show different pH values when measurements are made, either with the hydrogen electrode or by the inversion of sucrose. The amount of water held by clays under similar conditions will vary according to the hydration capacity of the cation held by the clay. The plasticity and shrinkage-on-drying of clays is found to go hand in hand with the hydration. The pore size of the clay particles has been found to be somewhere between 3Å and 5Å.

It remains to be considered whether the quantitative comparison holds between permutite and cellulose, as regards milli- equivalents of base exchanged per gram of clay and cellulose respectively. For artificial permutites Wiegner gives figures ranging from 0.46 to 1.0 milli-equivalents of calcium per gram of clay. It appears that the natural clays behave similarly. It is

very difficult to get any sort of reliable figures for cellulose. Edge gives a number of figures for cotton, sulphate and sulphite pulps. As is to be expected the acid treated pulps give the lower ash values. Edge treats the pulps with acid and alkaline solutions, and measures the adsorption of acid or alkali by its disappearance from solution, and he also determines the final alkalinity of the ash of the pulp. The sum of the final alkalinity of the ash and the adsorption alkalinity he finds to be sensibly constant in the case of any one pulp. Thus the adsorption depends on the original ash content of the pulp. But this does not prove that the cellulose itself is inactive. The argument in favour of the permutoid characteristics of cellulose may be presented in the following way.

Let us take first the case of Wiegner's clay, of which 1 gram has a base-exchange figure of 0.5 milliequivalents of calcium. We assume that the anhydrous clay substance has the composition $3SiO_2.Al_2O_3$, and that the calcium is replacing aluminium. Then the above calcium will correspond to 0.024gms of anhydrous clay. To obtain a comparison with cellulose, it is desirable to express the replaceable base in terms of the ionisable hydration water of the clay. The 'combined' water of clays varies a great deal. I refer to the water which, if removed, would cause the clay to lose its permutoid property. In this case it may be from 12 to 20%. If the actual figure selected be 12½%, the ratio of the total combined water in the clay to that part of it which, when ionised, is equivalent to the calcium

exchanged, will be about 28 : 1. Edge's figures for cotton cellulose may be selected for comparison. In this case 50 grams of pulp gave about 0.19 grams of ash, the alkalinity of which (all replaceable) was equivalent to about 40cc. of $N/_{10}$ acid. If the replaceable alkalinity were held to be due to the fixation of a kind of mineral permutite on the fibre, and the same composition is assumed as for Wiegner's clay, the actual weight of anhydrous permutite works out at about 0,19gm. and is equal to the actual ash weight. No permutite is known which has all its basic constituents exchangeable. Supposing now that each $(C_6H_{10}O_5)$ group of the fibre has one exchangeable hydroxyl group, the 50 grams of pulp will contain about 5.5 grams of water corresponding to the 'combined' water of the clay. The replaceable alkalinity of the pulp, if calculated to its equivalent as 'active' water, will correspond to about 0.036 grams. (Strictly we should calculate in terms of hydrogen or hydroxyl ions, but the result is the same). In the case of cellulose, therefore, the ratio of potentially active to replaceable water will be that of 5,5 to 0,036, or about 150 to 1, which is of the same order as for permutites. It appears probable, therefore, that the cellulose substance itself is a 'permutoid', and that the property does not reside in the ash content or in the membrane substance of Lüdtke. It is not forgotten that Kullgren found the adsorption of copper from solution to be related to the presence of sulphur residues in the sulphite cellulose, and that analogous facts have been discoverd by other experimenters. The difficulty

of removing these residues may well be due to the permutoid character of cellulose. The correspondence of the unit crystallite dimensions of cellulose with Wiegner's figures for the pore dimensions of permutites is another fact of interest. The acid suspension effect is a well known phenomenon, which makes it a very difficult matter to determine the hydrogen ion concentration of finished papers,[68] or of beaten pulps. The subject cannot be pursued any further here, owing to an almost complete lack of data. It would be very desirable to know if the base-exchange property followed the lyotrope series. The isoelectric point of cellulose suspensions might be determined by the transition from the acid to the alkaline suspension effect.

An instructive parallel is to be found in the case of the adsorptive power of activated charcoal. E.J. Miller[69] has recently examined the adsorption of various compounds including inorganic acids, bases and salts by a specially purified, ash-free, activated charcoal and finds, that in the case of inorganic salts hydrolysis occurs and the cation alone is adsorbed as a rule. The Langmuir-Harkins theory is verified and the adsorption is polar in character. The purified charcoal does not show an iso-electric point at all. In the case of organic acids the adsorption is partly hydrolytic and partly molecular. The case of cellulose remains somewhat disputable, and is obviously different from that of active charcoal owing to the known presence of unsaturated secondary valencies. In the papermaker's

beater certain ash constituents remain, partly as the result of former processes of purification, and the cellulose undoubtedly exhibits base-exchange adsorption phenomena, which could be best studied on a suspension of beaten pulp.

4. It might also be suggested that cellulose, by virtue of its active hydroxyl groups, may be able to form very slightly ionised salts with acids and alkalis. If such phenomena play any part in 'wet beating' it is difficult to see how the hypothesis can be of any value in the present state of our knowledge. The swelling phenomena of cellulose will be treated in another section. R.O. Herzog has quite recently asserted that only when cellulose truly interacts with electrolytes can swelling be adequately explained. It appears to the writer that a close study of the base-exchange phenomena of cellulose is the first step in that direction.

R E F E R E N C E S.

IV.

50 Cellulose criteria of purity:-
H. Hibbert, Ind.Eng.Chem. 15.748.(1923)
S.M. Neale, J.S.C.I. 50.177T.(1931) for $Ba(OH)_2$ method.
Birtwell and others, J.Text.Inst. 21.85T.(1930) (Copper number)

51 L. Kalb u. F. von Falkenhausen, Ber 60.2514.(1927)

52 P. Waentig, Cellulose Chemie, 10.81.(1929)

53 G. Kita, J.S.C.I. Japan, 33.142.(1930)

54 C.G. Schwalbe,(with Becker) Z.Angew.Chem.32.265.(1919)
also Z.Angew.Chem.32.355.(1919)
C.Z.74.(1920), W.B.51.(1920), P.Z. 53.(1920)
P.F.22.77 and 2662 (1924); 25.481.(1927)
Z.P.4.115.(1924)

55 Patents referred to in 54 above and
C.G. Schwalbe, Ger.Pat. 379,996 &
B Abstr. J.S.C.I. 1172 (1923)
H.P. Bassett, U.S.Pat. 1,792,351 &
B Abstr. J.S.C.I. 967 (1931)
C.G. Schwalbe, Ger.Pat. 456,929 &
B Abstr. J.S.C.I. 184 (1930)
Olsen and Aaronson, Ind.Eng.Chem. 21,1178(1929)

56 M. Nakano, J.Cell.Inst.Tok. 6.75,89,106 (1930)
See also Kienzl u. Nagl P.F. 28, 49.(1930) who more or less agree with Nakano, that strong acid pretreatment is bad and weak acid is useless, as far as the strength of the beaten sheet is concerned

57 J.E. Minor, Ind.Eng.Chem. 13.131.(1921).

58 H. Wiscilenus u. W. Gierisch, Koll.Z. 34.169.(1924)

59 P. Karrer, Koll.Z. 52,304.(1930)

60 See R.E. Liesegang, W.B.25, Beilage Technologie No.5 (1928) who quotes Herzfeld u. Klinger on albumen, and also claims that Hess regards oxycellulose as unchanged fibres surrounded by a film of alkali-soluble and degenerated cellulose.

61 See 54 and C.G. Schwalbe u. G. Teschner, P.F. 23. fest.ausl.heft. 144.(1925).
C.G. Schwalbe u. G.A. Feldtmann, P.F.23,589(1925)
C.G. Schwalbe, Z.angew.Chem. 37.125.(1924)

62 A. Tingle, Ind.Eng.Chem. 14.198.(1922)

63 K. Kanamaru, J.Cell.Inst.Tok. 4.259.(1928)

64 H. Rochier, P.F. 26.757 (1928)

65 S.R.H. Edge, J.S.C.I. 48.118T (1929)

66 Kullgren, Svensk.Kem.Tidsk. 42.179 (1930); 43.99(1931)
See also E. Oeman, P.F. 23.725,745,800,813(1925)
P.F. 25.642.(1927) and
H. Masters, T.Chem Soc. 121.2026.(1922)
See also reference in Koll.Z. 28.94.(1921)
Rona u. Michaelis who deny adsorptive power to be inherent in pure cellulose.

67 G. Wiegner, J.S.C.I. 50.65T and 103T (1931)

68 Schleicher u. Rössler, P.F. 22.205.(1924);
Schultze, P.F. 26.625.(1928);
also P.M.A. Tech.Sec.Abstracts(May 1927.)

69 E.J. Miller, 5th. Coll.Symp,Mon. Michigan,U.S.A. (1927) p.55.

V.

PROPERTIES OF SUSPENSIONS OF BEATEN FIBRES.

1. The properties of a suspension of beaten fibres may be considerably modified by the degree of sub-division. Owing to the orientation of the micelles in the fibrillae, and the almost parallel arrangement of the latter in the fibre, it is clear that different effects may be expected from transverse cutting and longitudinal splitting into fibrillae. The actual dimensions of the papermaking fibres are quoted in several standard works on the industry. A good representative collection of data is contained in a paper by Huebner[70] on the adsorption of dyes in the course of beating. It is generally conceded that the Esparto fibre is not usually cut during beating. The minimum fibre length during quite severe beating may be roughly taken as 0.2 mm. It can be readily shown that the increase in outer specific surface of the papermaking fibres is little affected by cutting and much more by fibrillation.

We may take the case of a broken-in cotton half-stuff of fibre length 2 mm. and diameter 0.02 mm. If we assume the fibre to be cylindrical, we find the volume to be 63×10^{-8} cc.

1 gram cellulose with 25% air space will occupy 1.2 cc.

Hence there will be 1.9×10^{6} fibres per gram.

Fibre uncut will have a specific surface of 0.24 sq.M/gram.

Fibre cut 10 times - " " " 0.24 " " "

" split 16 " - " " " 0.96 " " "

" " 1024 " - " " " 7.64 " " "

The last case would correspond to the external surface of a fibre which had been completely resolved into fibrillae.[45] Strachan[36] has also considered the increase of specific surface and gives somewhat higher figures. As the increase of specific surface is directly proportional to the diminution in diameter of long fibrous bodies, it is clear from the dimensions of the unit micelle given on page 29 of this paper, that it is theoretically possible, without destruction of the micelle, for the specific surface to reach values of 1000 sq. M. per gram. At such a degree of dispersion the colloidal properties of the cellulose would be profoundly altered. As the external specific surface during the course of beating is seldom likely to exceed 10 or 20 times that of the unbeaten fibre, great changes in physico-chemical properties are unlikely to be due to this cause alone. Strachan, it is true, considers that the increase may be one hundred-fold, but this seems a high figure. Freundlich[71] quotes a figure of 200 sq. M. per gram for the specific surface of animal charcoal, and the means of arriving at this result will be dealt with later. The variation of fibre-length with beating has been measured by Beadle[72] and others. The mechanical theory of beating as developed by Smith[5] depends on the fact, that the beater bars in their motion through the stuff take up a coating of fibres, or a 'fibrage,' which varies in amount with the average fibre length. Smith quotes figures for this, and Jacobson[73] has recommended a

tester for beating degree, based on the principle of drawing a standard rod through a pulp of standard fibre content at a standard velocity. He obtains figures which show a decrease from 260 to 40 units for rag beating. There is no practical method of determining the degree of fibrillation, and therefore the method of direct measurement of dimensions must be held to fail, as regards the obtaining of accurate knowledge of specific surface changes in the course of beating.

Attempts have also been made to measure the beating degree by the diminution of the apparent viscosity of the pulp suspension during the course of beating. Jupeau[74] recommends a 'finometer' for the beating of the pulp for nitrocellulose, which consists of a lead sphere suspended by a wire in the trough of the beater. The travel of the stuff causes the wire to assume an inclination to the vertical, and the tangent of the angle of inclination has been taken as a measure of fineness. It is difficult to see how viscosity methods can be of much value, even with well beaten stuff. The viscosity of the suspension must depend on the fibre dimension, fibre shape, and perhaps also on the hydration water envelope of the fibres.

2. More success has been obtained by measuring the drainage properties of beaten stock. The method has a very practical origin. The apparatus is always to some extent a replica of the 'wire' part of the paper-machine. One of the most important effects of beating is the modification of the rate at which the pulp will

part with its water of suspension on the machine wire and the suction boxes. The ease of drainage, or 'freeness' of a stock is diminished by subdivision of the fibre,[75] and by the undefined property of wetness, greasiness or hydration. A 'freeness' or 'wetness' tester will not distinguish between these two phenomena. The apparatus is usually a cylindrical container which can be filled with dilute pulp. The bottom is a wire sieve of standard mesh and area. In the older testers the volume of drainage through the wire was measured during definite time intervals, and rate-of-flow curves were constructed, from which inferences could be drawn as to the two factors of beating. E.W.L. Skark[75] prefers this older type of Schopper tester; in another paper he recommends a 'stuff spindle' or hollow tube with a wire sieve bottom, which is floated on the pulp suspension, the length of time being noted until the apparatus sinks owing to upward filtration of water through the wire sieve. As it will be necessary to refer later to some recent investigations on beating by Nakano[76] in Japan, his 'beating degree' tester will be briefly described here. He uses a 250 cc. glass vessel of 6 cms. diameter, the bottom being covered with wire gauze. There is an air cock fitted to the top of the vessel, and a close-fitting lid to the bottom. A suspension of 1 gram dry weight of beaten pulp in 200 cc. of water at 20°C. is used, and the number of seconds is noted for the drainage of 100 cc. water. This number is defined as the 'beating degree' of the

pulp. The arrangement of bottom cover and air cock allows the drainage operation to be initiated suddenly, after the pulp suspension has been properly shaken up.

The newer 'freeness' testers have also used a device of this sort, but their great practical advantage consists in the elimination of the time measurement altogether. There are several types on the market. In America the Green and Williams testers are in use. Davis[77] has published several articles dealing with the use of the Williams tester. The Pulp Evaluation Committee of the Technical Section of the British Papermakers' Association[78] recommends a tester of the Green type. In Europe the improved Schopper-Riegler tester is in common use, and, except for special experiments, it has been used as a comparative standard for beaten pulps throughout the present investigation. As will be seen from the diagram, the drainage water is divided into two parts. A part will drain under a constant small head through the lower narrow orifice, and the other part will overflow by the large side orifice. In practice 2 grams of dry pulp are used, suspended in 1000 cc. of water. The plug is raised, and the amount draining rapidly through the side orifice is measured. This is the 'freeness' water. The 'beating degree' or 'wetness' is taken to be -

$$1/10\ (1000 - \text{freeness water in cc.})$$

The instrument is rapid and definite in its action. It is easy to correct for small deviations in the weight of pulp used, and the temperature coefficient

is very small. Some results obtained with the instrument, and corrections required, can be found in a paper by E.J. Guild and S. Mills.(79) It is obvious of course that the sensitivity of the instrument is at a maximum if the 'freeness' water is about 500 cc., and that for very 'wet beaten' pulps the instrument is hardly sensitive at all. As a matter of fact it is almost impossible to obtain a wetness reading of over 96^{0} with any stuff, however carefully beaten. In the study of the suspension properties of beaten fibres, the finest fibrillae and fibre debris are of the greatest interest, and a great proportion of these are inactive when testing with the Schopper-Riegler instrument. The finest fibrillae do not yet form part of the filtering cake, by the time that the drainage of the 'freeness' water is already complete. The fitting of a finer nozzle for the slow drainage water might overcome this defect, but in practice another method has been selected in the experimental part of this paper. It will be obvious of course, that, as far as any of the practical testers go, neither 'freeness' nor 'wetness' is an additive or alligative property of pulps. The main disadvantages of the practical testers from the point of view of research may be summed up as follows:-

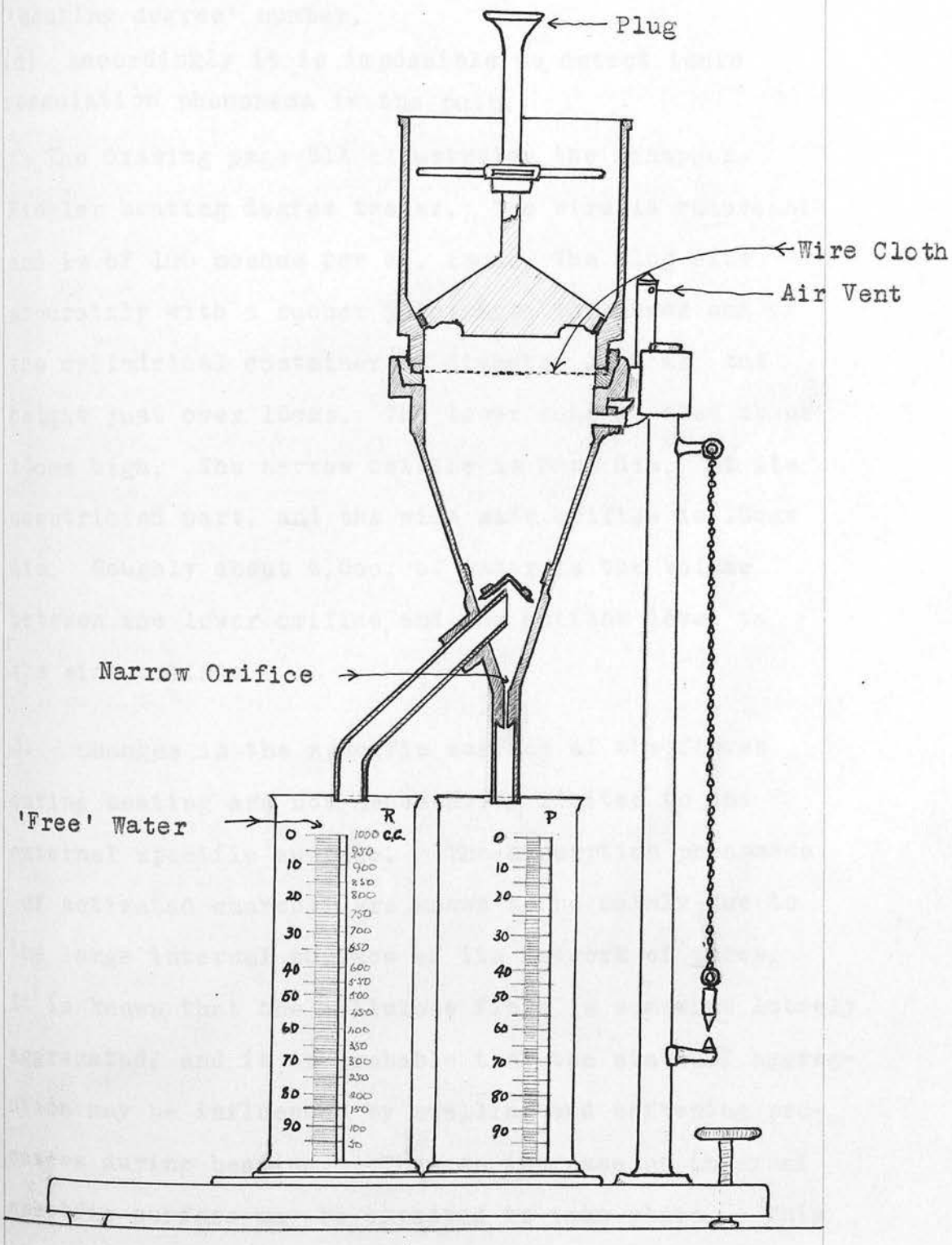
(a) A complicated law connects the 'beating degree' and the weight of pulp used.

(b) There is no simple connection between 'beating degree' and the viscosity of the suspension medium.

(c) The finer fibres, fibrillae and fibre debris, which

S C H O P P E R - R I E G L E R

Beating Tester.



may be expected to show the most colloidal behaviour, have a disproportionately small influence on the 'beating degree' number.

(d) Accordingly it is impossible to detect ionic coagulation phenomena in the pulp.

The drawing page 51A illustrates the Schopper-Riegler beating degree tester. The wire is removeable and is of 100 meshes per sq. inch. The plug fits accurately with a rubber joint into the lower end of the cylindrical container of diameter 13.6cms. and height just over 15cms. The lower cone is also about 15cms high. The narrow orifice is 2mm. dia. at its constricted part, and the wide side orifice is 18cms. dia. Roughly about 4.5cc. of water is the volume between the lower orifice and the outflow level to the side orifice.

3. Changes in the specific surface of the fibres during beating are not necessarily limited to the external specific surface. The adsorption phenomena of activated charcoal are known to be mainly due to the large internal surface of its network of pores. It is known that the cellulose fibre is somewhat loosely aggregated, and it is probable that the state of aggregation may be influenced by swelling and softening processes during beating. Thus an increase of internal specific surface may be expected to take place. This could only be measured by the adsorption method, but the question is very complicated. In the case of capillary-active solutes the adsorption may be non-polar and may

therefore follow the Gibbs surface-excess equation in its simple form -

$$u = \frac{-c}{RT} \cdot \frac{d\sigma}{dc}$$ Freundlich(80) p.169.

u = Surface excess of solute.
c = Equilibrium concentration of solute in solution.

Unfortunately $\frac{d\sigma}{dc}$ the rate of change of surface tension with concentration, at the solid-liquid interface cannot be measured. If dilute solutions are used, and the solute forms a true solution without appreciable ionisation, the conditions of non-polar adsorption may be realised. The above equation will then enable a comparison to be made of the active surfaces of two adsorbents. The same end would be equally well attained by using the usual empirical adsorption isotherm -

$$\frac{x}{m} = ac^{\frac{1}{n}}$$ Freundlich(80) p.172.

x = weight of substance adsorbed.
m = " " adsorbent.
n is a constant for the particular solute and solvent used.
a depends on the adsorbent also, and is a constant for each particular case.

This equation can be used to compare the specific surface of two adsorbents if conditions are chosen so that a and n are alike in the two cases. Confirmative tests would be available if different solutes and solvents were used. The great difficulty, however, lies in the potential reactivity of the hydroxyl groups of the cellulose molecule. In most cases polar adsorption and even secondary reactions may occur, as is evidenced by the variegated character of dyeing phenomena.

In many cases the adsorption isotherm is followed for low concentrations of solute whereas a saturation

limit of adsorption is reached at higher concentrations. In the case of cellulose most solutes are sufficiently polar in character to orientate themselves on the fibre in accordance with the ideas of Hardy, Langmuir and Harkins.(81) A saturation limit of adsorption may then be expected when the surface residual valencies of the cellulose have been satisfied. Generally speaking, this would mean a unimolecular surface layer of adsorbed substance, but as McBain(82) showed for solutions of sodium oleate, thicker surface films and perhaps chains of oriented molecules are possible. Freundlich(83) in a recent book discusses the extent and change of surface of colloidal systems from this point of view. It appears that Paneth was able to determine the specific surface of microcrystalline lead sulphate by a radio-active method, and that dyestuffs were adsorbed by lead sulphate with formation of a unimolecular layer. Paneth considered that the formation of a unimolecular layer of the adsorbed substance was quite characteristic where saturation adsorption occurred, and in this way he determined the already quoted figure for the specific surface of animal charcoal. Bancroft(84) has recently shown that the adsorption of methylene blue by lead sulphate varies greatly with the pH value of the solution, so that comparison of the specific surface of beaten and unbeaten fibres can only be of value if all the experimental conditions are rigidly controlled.

Huebner's(70) results on the adsorption of Night Blue by cotton and artificial silk fibres are not very

hopeful as quantitative measures of specific surface. He obtains adsorption maxima which are hardly affected by 6 hours' beating treatment of cotton fibres, and which show no proportionality to the apparent specific surface of the two varieties of artificial silk which he used. Artificial silk threads are certainly of most irregular cross-sectional form in many cases, and apparent specific surface estimated from measurements of diameter may be no true guide. Night blue is a hydrophilic colloid which may have a large envelope of hydration water, as its diffusion coefficient is extremely small, although the molecular weight is only 575. The dyestuff may not be able to penetrate the finer pores of the fibre.

The base-exchange characteristics of cellulose might vitiate any results obtained by the adsorption of ionised solutes. The resultant equilibrium would probably be a function of the concentration, but it is unlikely that it would follow the adsorption isotherm. In some cases it would be determined by the law of mass action, and would be dependent on the degree of hydration of the exchanging ions. In other cases considerations of ionisation, hydrolysis and solubility would determine the equilibrium.(67) Such phenomena occur during the adsorption of inorganic salts by activated charcoal, whereas in the case of some organic substances both molecular and ionic adsorption occur.(69) If true hydration of the fibres takes place, negative adsorption may be found with certain concentrated solutions, as the

result of the partition of the water between the hydrated fibre and the solute. This will be discussed in a later section. Sufficient has been written here to show the complexity of the adsorption phenomena of cellulose. In the earlier part of the experimental investigation which follows, a number of experiments on the adsorptive powers of beaten and unbeaten cellulose were tried, but the results were unsatisfactory, and the matter was not pursued any further.

4. Adsorption effects should be greatly influenced by any electric charge on the fibre particles. In accordance with Coehn's rule fibres take an electronegative charge in pure water. The magnitude of the charge depends on the pH value of the aqueous solution, as was shown by Harrison's[85] work on the electrokinetic potential of cotton fibres. A.J. Stamm[86] recently discussed the question of the isoelectric point of fibres, and he argues that if it exists at all, it must be at a fairly high concentration of acid. Many other investigators[87] have examined the question and most conflicting results have been obtained. Many colloids show a considerable shift of the isoelectric point on the addition of neutral salts.[88] Morgan and Libby[89] have recently endeavoured to correlate beating effect with varying pH value of the solution in which the beating has been conducted. Their assessment of beating degree is based on the strength of the sheet of paper made from the beaten pulp, and to a lesser extent on drainage properties. They have found minima of

beating effect at pH values 4.5, 5.5 and 10.5 for cotton and 8.5 for sulphite wood fibres, with intervening maxima at pH values of 5.0 and 8.5 for cotton and 7 and 10.5 for wood. Sodium carbonate and acetic acid were used to vary the pH value. It seems that the solutions were not buffered. It is extremely difficult to find any satisfactory interpretation of their results. It may well be the case that cellulose fibres, like activated charcoal,[69] do not show an isoelectric point at all, and that selective adsorption and chemical degradation play a considerable part in the results of Morgan and Libby.

It would be of interest to know how the behaviour of cellulose fibre suspensions contrasts with that of the general class of suspenoids and emulsoids in an aqueous medium. A certain amount of information could be obtained in this way which might indicate whether true hydration of the fibre actually takes place during the beating operation. In the experimental part of this paper it will be shown that suspensions of beaten cellulose fibres are very sensitive to electrolytes in solution, and exhibit what appear to be coagulation phenomena, which are quite analogous to the precipitation of suspensoïds. The influence of the cation is predominant, and the valency effect is fairly marked and somewhat along the lines of the Schultze-Hardy precipitation rule. The function of alum in partially 'freeing' a stock on the papermachine wire is the practical side of the same phenomenon. At the same time, it must be

admitted that such phenomena are probably of far greater importance in the sphere of sizing than of beating paper pulp. Such ionic coagulation effects may be interpreted in terms of alteration of pore size of the fibre cake, but any estimation of pore size based on drainage tests would be of doubtful validity. With electrically charged fibres the drainage rate will not be in accordance with Poiseuille's law, and the electroviscous effect as evaluated by Smoluchowsky[90] may be expected to play a part. Ionic coagulation phenomena in the case of beaten fibres may therefore indicate any or all three effects - alteration of pore size, diminution of fibre charge with reduction of electroviscous effect and lastly actual dehydration.

Of recent years an enormous amount of work has been done on the electrokinetic potential and surface conduction at the cellulose-water interface. The work has also been extended to the variation of these properties during the course of beating. The older theory of electrokinetic potential is based on the idea of the Helmholtz double layer. Of recent years the theory has been considerably modified, but it cannot be said to be satisfactory yet, so long as the exact nature of the water adsorption layer at the interface is not known. Most of the recent work on the general nature of the electrokinetic potential and surface conductance phenomena at the cellulose-water interface will be found in several recent papers by R.A. Gortner and D.R. Briggs.

The electrokinetic potential ζ according to the Helmholtz theory varies as $\frac{de}{D}$

d = thickness of double layer.
D = dielectric constant of the medium in the double layer.
e = charge per unit surface.

Briggs has selected cellulose for experiment, because he considers it to be an inert substance which does not become electrically charged either by attracting ions by the force of residual valency, or by splitting off ions by dissociation.(91) It is unlikely that this is altogether correct. The dielectric constant within the double layer need not be the same as in the bulk of the liquid. Briggs points out that an exceedingly strong electric field will lower the constant considerably, and that such fields must exist in an excessively thin double layer. Errera(92) in a recent discussion states that the dielectric constant may fall from a value of 80 to a value of 2 or 3 in the 'bound' water of colloids. The thickness of the double layer may be variable, especially if hydration phenomena occur. In the case of permutites Wiegner(67) identifies the double layer with the hydration envelope. It is doubtful if this would be valid for cellulose. If the origin of the charge were related to adsorbed ions (by a base exchange) the surface density of charge might decrease with subdivision. The effect of the size of quartz particles on the ζ potential has been investigated by Bull and Gortner,(93) and it has been found that within certain limits ζ diminishes according to the cube of the diameter, the smaller particles having lower values. The polarity

of unsymmetrical nature of the liquid is of great importance, as Martin and Gortner[94] have found in the case of organic liquids. It seems highly probable therefore, that the water double layer is an oriented one at the cellulose interface.

In the case of surface conductance Briggs[95] has shown that the original Smoluchowsky equation does not hold, and that the phenomena can only be explained by assuming that the surface layer of water on the cellulose is different from the bulk of the liquid as regards conductivity. In this case Bancroft's[96] suggestion is adopted, that the surface layer consists of monohydrol (H_2O) as against the polyhydrol $(H_2O)_n$ in the bulk of the liquid. Bull and Gortner[97] have been able to distinguish between changes in the charge of the particles and in the thickness of the double layer. They have worked with various aqueous salt solutions at the cellulose-water interface. They conclude that $\underline{e}$ may increase at the same time as ζ decreases, and that the decrease of $\underline{d}$ is the important factor. They admit however that $\underline{e}$ decreases with adsorption of polyvalent ions, and in the case of $Th^{\cdots\cdot}$ $\underline{e}$ may even be reversed. Briggs[95] does not find that surface conductance is a function of electrokinetic potential at all. He considers however, that it is a valuable measure of specific surface or colloidality.

From the foregoing rather cursory survey of the work which has recently been done on these lines, it should be obvious that it is a very unwise thing to

draw conclusions as to changes in hydration, or as to specific surface during beating from measurements of electrokinetic potential and surface conductance. It is necessary however to review some work which has been done by Kanamaru[98] on this question. He finds that electrokinetic potential decreases in the course of beating according to a unimolecular reaction law

$$\frac{d\zeta}{dt} = -a(\zeta - \zeta_\infty) \qquad \begin{matrix} t = \text{time.} \\ a = \text{constant.} \end{matrix}$$

Kanamaru equates 'beating degree' with hydration, and assumes that the decrease is a measure of hydration. It should be mentioned that Briggs notes the same phenomenon, and finds that it has been also reported to occur with glass powder on steeping in water. Both Briggs and Kanamaru report that it occurs with cellulose on steeping, as well as during beating. Kanamaru has pursued the matter further, and finds that on prolonged steeping the ζ value again commences to rise. The rise commences at once if the pulp is first boiled in water and then cooled. Kanamaru interprets this by assuming that the boiling process completes the hydration very quickly. The subsequent rise in ζ value he attributes to syneresis dehydration. By contrast, Nakano[99] considers that imbibition water is removed by boiling in water. Kanamaru finds that both steeping and beating gradually increase the surface conductance according to the equation -

$$\frac{dK}{dt} = \frac{C}{t}(K - K_o) \qquad \begin{matrix} (K_o = \text{surface conductance at} \\ (C = \text{a constant} \quad (\text{the start.} \end{matrix}$$

The value of K seems to increase on steeping, regardless of whether a previous boiling process has taken

place or not. Kanamaru's interpretations of his experimental work are obviously vitiated by the incomplete knowledge available, as to the true nature of the ζ and $\underline{K}$ values and their significance. It is expedient to postpone further discussion of the matter until after the experimental section of this paper.

5. It is to be expected that beaten fibre suspensions will afford some indication of the hydration which is supposed to occur during beating. Many colloids show a lyophobic character under some circumstances and a lyophilic character under others. Colloidal ferric hydroxide is a case in point. By the desiccation of a ferric hydroxide sol a film or pectograph[100] can be obtained consisting of long fibrils (the lyophobic element) and a continuous inter-fibrillar cement (the lyophilic element). W.W. Taylor[101] has recently shown how ferric hydroxide sols react to the well-known lyotrope series of ions. Failure to respond to the lyotrope series in the matter of precipitation can hardly be taken as a proof that hydration does not occur, especially in the case of beaten fibre suspensions which are very sensitive to the effect of the cation of the added electrolyte.

The most significant investigations in this field have been recently carried out by H.R. Kruyt[102] and coworkers. Kruyt has investigated the conditions of stability of the lyophilic colloids, and concludes that there are two factors, each of which in itself is sufficient to stabilise the colloid, i.e. electric charge

and hydration envelope. He points out that the degree of dispersion of such colloids as agar and gelatine is not particularly high, and that dehydration can be effected in two ways, (a) by abstracting the hydration envelope by the addition of strongly hygroscopic liquids such as alcohol or acetone, (b) by the polar adsorption of such a substance as tannic acid, which will then present a hydrophobic surface to the solution. It is possible by means of the drainage tester of the author to investigate the dehydrating effect of alcohol on beaten cellulose suspensions. The effect is quite considerable. A comparison case using a non-hydrated fibrous substance, such as well disintegrated asbestos, affords an interesting contrast. Such phenomena will be dealt with in the experimental part of this paper.

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VI.

THE GEL PROPERTIES OF BEATEN FIBRES.

The changes produced by the beating operation also manifest themselves in what may be called the gel properties of the fibres in a water-wetted state. Such properties as the vapour pressure of moist fibres, the heat of wetting, the volume change on wetting, and the cohesion of moist fibres which later manifests itself in the cohesion of the dried sheet of paper, fall into this category. The outstanding question is the manner in which the water is bound to the fibres. As in many cases of lyophilic colloids, there is little point in the clear-cut distinction of chemically and physically bound water. No combination of fibre and water in exact stoichiometric ratios is known to exist, and the question is rather one of the extent to which water is bound to the fibre by loose capillary forces, or by the stronger partial valency forces, which are characteristic of the binding of imbibition water by lyophilic colloids such as gelatine.

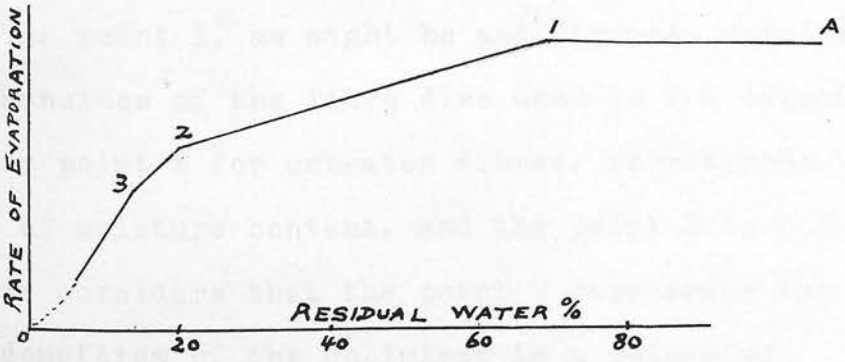
1. The change of vapour pressure of moist cellulose fibres with increasing water content has been measured by many workers.(103) It is known that the vapour pressure isotherm is a continuous curve, although a hysteresis effect is noticeable to some extent. The vapour-pressure is usually represented as a fraction of the pressure at a free water surface at the same temperature. The curve then illustrates the relation between relative humidity and water-of-condition of the

fibres. In the case of paper sheets corresponding relations have been found between relative humidity and strength properties, and such relations within a mean range of temperature are almost independent of temperature. A marked degree of hysteresis occurs when the fibres are almost desiccated, especially at temperatures of 100°C. and over. The advantage of using slush pulps rather than dried pulps for the making of strong papers, is due to this cause. With very 'wet beaten' pulps the hysteresis is more pronounced.

Pidgeon and Maass[104] have made an accurate study of the vapour pressure isotherm for wood fibres. They worked in vacuo in an enclosed system, with the fibres suspended permanently on helical quartz threads, for continuous weighing. The humidity was varied by altering the temperature of a water vapour supply bulb which was maintained at a lower temperature than the rest of the apparatus. Reputed errors due to non-condensible gases were avoided. They conclude that 1 - 2% water is strongly held, but is reversibly adsorbed. From 2 - 10% water content they believe the fibre capillaries are being filled, and above 10% the adsorption is slight. They conclude that gelatine behaves in a similar manner. Recently Seborg and Stamm[105] have used a similar type of apparatus, and have extended the investigation to beaten fibres. They worked in air, and controlled the humidity by circulating the air over different concentrated salt solutions. Their results were in agreement with those of Pidgeon and Maass, and showed an

unbroken vapour-pressure curve of characteristic sigmoid shape. Hysteresis was shown to have no connection with residual non-condensible gases. Beating of the fibres did not affect the vapour-pressure curve. They conclude that the fibre-water relationship is a sorption* phenomenon, and that there is no evidence of fibre-water bonding. Some further experiments by the same authors on the surface conductance of moist cellulose led to the same conclusion.

2. Several workers have investigated the rate of evaporation of water from the surface of moist porous materials. E.A. Fisher(106) has made a study of this for wool, sand and clay. The evaporation was conducted in a desiccator over concentrated H_2SO_4, and the material was weighed at intervals. Thus a curve connecting time of evaporation and percentage of residual moisture was obtained. From this curve, by a geometrical differentiation method, a curve connecting rate of evaporation with residual water was constructed. The latter curve was always found to consist of a number of straight line portions (usually 3 and on one occasion 4) similar to those of the accompanying diagram.



The straight line portion A1 corresponds to a constant maximum rate of evaporation from the free-water surface

* 'Sorption' is used to imply a loose physical union of fibre and water, the exact nature of which is unknown.

of the completely wetted material. The portion 12 corresponds to a uniformly diminishing rate of evaporation, although the point 2 corresponds to the saturation vapour-pressure of the completely wetted substance, as far as the residual water content is concerned, in the case of wool fibre at any rate. It is concluded therefore that the reduction in rate of evaporation along the line 12 is due to a slowing down of the diffusion of water from the interior of the substance to the surface, and not to any capillary binding of water by the gel. Between the origin and point 2 capillary forces are active. In a review of the literature on water binding in colloidal systems A. Kuhn(107) describes a freezing point dilatometer method, which shows that in the case of wet sand all the water is free, and that none is capillary-bound. Wet sand was one of the substances used by Fisher, which gave three change points in the rate of evaporation curve.

The method of Fisher has been applied by J.W. Rowe(108) to the study of beating phenomena. Rowe finds three points of change of direction in the rate of evaporation curve. The point 1, as might be anticipated, depends on the dimensions of the fibre disc used in the experiment. The point 2 for unbeaten fibres, corresponds to about 20% of moisture content, and the point 3 to under 12%. Rowe considers that the point 2 represents the water-of-condition of the cellulose in a saturated atmosphere, although he finds that beating increases the moisture content at point 2. Rowe assumes that

point 3 corresponds to the percentage of water of hydration. With the progress of beating the water content at point 3 also increases, as also does the difference in moisture contents at points 2 and 3, which is attributed by Rowe to water held by surface forces. The rise in moisture content is not uniform with the progress of beating for the points 2 and 3. In both cases the rise is to a maximum, with a subsequent uniform fall. If beaten stuff is steeped in water the fall proceeds steadily. The behaviour is curiously similar to the observations by Kanamaru[98] on electrokinetic potential. It is difficult to avoid the conclusion that the electrical charge of the fibre is the active cause, in so far as it may affect the transfer of water by diffusion from the interior to the sruface of the cake. A change in the drainage properties of the beaten fibre with steeping in water, and the change which takes place on boiling with water and subsequent cooling, are on the same lines, yet if the treated pulp be made into sheets of paper, no sign of change can be found in the mechanical qualities of the finished sheet. If hydration is conceived as the formation of a colloidal surface film, or surface film of fibre rendered cohesive in some way through the agency of the wetting liquid (see p.71), and which will later promote the mutual bonding of the fibres in the dry state, then it is unlikely that the changes observed by Rowe and Kanamaru fall into this category at all, and the rate of evaporation method fails as a means of studying hydration during beating.

Rowe performed no experiments by the static method on the water-of-condition of beaten pulp, and there is

no reason to doubt the conclusion of Seborg and Stamm that no change in this property takes place during beating. In that case it is difficult to interpret point 2 on Rowe's curves, as it varies enormously with beating. From certain experiments done by the author on very well beaten pulps it is clear that the almost dried cake becomes so close and horny in texture, that diffusion from the interior to the surface becomes extremely slow and the surface rate of evaporation does not affect the true rate of evaporation at all. It is noteworthy that Schwalbe[61] has also given up the idea of measuring the progress of beating by the moisture-of-condition of the beaten stuff, even in the case of structureless mucilage.

3. One of the main objects of the beating operation is to impart increased strength to the finished sheet of paper. As has been said previously (III page 23), many investigators have postulated the existence of a colloidal surface film of a cement-like substance between the fibres. Papermakers know that there is some additional strength factor in a sheet of paper, over and above the mechanical felting of the fibres on the wire and in the presses. Nakano[109] describes a series of sheet-making experiments using wool, silk and asbestos fibres. Wool does not fibrillate nor does it form a sheet. Silk and asbestos split up into fibrillae, felt well enough and form sheets which, however, have no strength, owing to the free slippage of the fibres. Vegetable fibres alone have the colloidal surface condition

which is essential to the formation of a strong sheet.

This surface cohesion is manifested with water but not with other liquids. Felting can undoubtedly take place in such liquids as alcohol, as will be shown later experimentally. It would appear then, that the surface of beaten cellulose fibres behaves as if it were covered with a film of adhesive, and it is well known that additional strength can be imparted to papers by the gelatine sizing process and by the addition of peptised viscose to the stuff. The surface layer of beaten fibres may then be held to resemble a swollen gel. If the process were carried on far enough, this gel would tend to fill up all the interstices between the fibres, and on drying a homogeneous sheet would be produced of greater strength, but of less elasticity than the unbeaten paper. The transparency and hardness of exceptionally well beaten papers confirm this expectation. Such a surface gel might be expected to show considerable shrinkage on drying, and any unevenness in drying would give rise to the well known cockling of wet-beaten papers with sudden change of atmospheric humidity. As far as the actual fibres are concerned there would also be a contraction on drying, but the lack of surface cohesion in an unbeaten or lightly beaten sheet would allow of the contraction occurring as far as the individual fibre is concerned, without the same degree of shrinkage on the part of the sheet of paper as a whole. In applying the analogy of the elastic gels such as gelatine to cellulose fibres, it

is as well therefore not to push the argument too far. Those investigators who have measured the swelling of cellulose fibres in water or weak aqueous solutions, e.g. Trogus[41], have noted a quite inconsiderable fibre shortening and an increase in diameter of only 10 - 30% as compared with 40 - 50% shortening and 1000% diameter increase for cuprammonium swelling. Even then the shape of the fibre makes such measurements of doubtful value as real measures of volume change. An estimate of increased cohesion between the fibres, due to the colloidal surface state would appear to be preferable as a measure of the gel-swelling effect during beating.

4. Considerable work has been done of recent years notably by von Weimarn[110] on the swelling and peptisation of cellulose fibres in concentrated aqueous salt solutions. As swelling is always a precursor of peptisation, a consideration of von Weimarn's work may throw some light on the surface swelling which probably takes place during beating. Von Weimarn claims that swelling will take place in a sufficiently concentrated solution of any neutral salt under the proper conditions, although peptisation may not always follow the swelling. It is interesting to note that he starts off in one method by a mechanical grinding process usually conducted at very low temperatures (liquid air or liquid CO_2) in order that the fibre may be brittle. In another method he conducts the preliminary swelling in relatively weak salt solutions at a moderate temperature. The final

swelling and peptisation are conducted in concentrated salt solutions at higher temperatures. The efficacy of different neutral salts varies a great deal. Generally speaking the desiderata are great solubility and hydration capacity on the part of the salt, and also considerable viscosity of the hot concentrated salt solution. The latter condition would accompany to some extent the capacity for hydration of the salt. Work done in Britain by H. Williams[111] shows that for peptisation to occur at atmospheric pressure, the solution must have a viscosity above a certain minimum value and a positive heat of dilution between certain well defined limits. Von Weimarn gives the order of efficacy of a number of salts, ranging from the thiocyanates, most of which peptise in concentrated boiling solutions at atmospheric pressure, to sodium chloride which, even at very high pressures and temperatures, and over prolonged periods of time only effects a limited amount of swelling and hardly any peptisation at all. To a considerable extent von Weimarn's arrangement of salts follows the well known lyotrope series, both for cations and anions. Von Weimarn has applied his methods to produce both films and threads of regenerated cellulose. The two main features of interest in his work as regards the beating problem are (a) The greater ease of swelling and subsequent peptisation after a preliminary mechanical treatment. (b) The need for very concentrated salt solutions and high temperatures for the process. Arguing from the results

of von Weimarn, it is hardly to be expected that any notable degree of swelling will take place at ordinary temperatures in weak aqueous solutions of salts, or that the addition of neutral salts in moderate quantity will greatly influence the course of beating. The latter deduction may not be entirely justified, as the action of moderately dilute neutral salt solutions before and during a severe beating process may indeed accomplish what neither cause acting by itself would have been able to do.

5. It is necessary now to pass on to some general considerations of the swelling phenomena of elastic gels. The laws which regulate the swelling of elastic gels in pure liquids have been worked out very fully by J.R.Katz(112) a good many years ago. In a recent paper he deals with the case of cellulose in particular. Freundlich in 'Capillary and Colloid Chemistry'(113) also goes into the matter very fully. Generally speaking, cellulose fibres come naturally under Freundlich's definition of an elastic gel. The swelling of cellulose occurs in water and in aqueous solutions, but not in such liquids as alcohols or hydrocarbons. It is natural therefore to regard cellulose fibres, when wetted with water, as a more or less swollen two-phase elastic gel.

The vapour-pressure isotherm of cellulose fibres (in this section the liquid referred to is to be understood as water in all cases) has been already discussed. It is similar in form to that for gelatine, and is of a characteristic sigmoid shape as in the diagram at the

end of this section. The curve is difficult to determine near the saturation point, but if the difficulties are satisfactorily overcome, it is probable that there would be no distinction between the amount of water taken up at the saturation point from aqueous vapour, and the water of imbibition taken up by immersing the fibres in liquid water. Katz admits however that a certain hysteresis occurs with cellulose fibres, and that the vapour pressure isotherm is not the same when the equilibrium is approached from opposite directions.

In order to press out swelling-water from a swollen elastic gel through a semi-permeable membrane a considerable pressure may be required. A definite equilibrium swelling pressure corresponds to a definite water content of the gel. Reinke in 1879 first determined the law connecting swelling pressure and concentration of water in the gel. Freundlich's expression is as follows:-

$$c = \frac{1000}{V_G + aV_F}$$

(c = concentration gms. dry gel in 1000 cc, (gel + liquid)
(a = wt. of water taken up by 1 gm. gel.
(V_G = specific volume of dry gel.
(V_F = specific volume of the liquid.

Then $P = P_o c^k$

(P = swelling pressure.
(P_o = swelling pressure when c = 1.
(k = constant.

For most swellable substances k has a value about 3. It is very difficult to measure swelling pressures when c becomes very large.

As the swelling under any definite pressure applied to a semi-permeable membrane separating the swellable gel

and the swelling liquid, is a reversible equilibrium, thermodynamic considerations may be applied to find a relation between swelling pressure and vapour pressure.

Katz, by the consideration of the equality of the energy effects due to the isothermal transference of a very small quantity of pure liquid through the membrane between two similar gels swollen to a slightly different degree, and its retransference in the opposite direction by a distillation process, has evolved the following equation:-

$$P = -\frac{RT}{MV_o} \log \frac{p}{p_s}$$

P and p are the swelling and vapour pressure of the gel.

M, V_o, p_s are the molecular weight, specific volume and vapour pressure of the pure liquid.

If the vapour pressure isotherm of the gel is known, the values of $\underline{P}$ are calculable from this equation. As $\underline{p}$ is very small near the dry point of the gel, $\underline{P}$ will be exceedingly large. Freundlich states that the observed values of $\underline{P}$ are always lower than the calculated ones, and he shows that in the case of a gelatine gel where the value $p/p_s = .020$, $P = 5000$ atmospheres. Similar values must hold in the case of cellulose fibres.

The free swelling of elastic gels is accompanied by a considerable evolution of heat. Katz expresses this by the equation:-

$$W = \frac{Ai}{B+i}$$

W = Heat evolution for the taking up of i gms water per gm. dry gel.

A, B are constants.

A more interesting figure is obtained by differentiation:-

$$\frac{dW}{di} = \frac{AB}{(B+i)^2} \qquad \text{also} \quad \left(\frac{dW}{di}\right)_{i=0} = \frac{A}{B}$$

The latter value Katz calls the 'first heat of swelling.' It is the heat evolved when 1 gram of water is taken up by a very large quantity of dry gel. It is approximately 200 - 400 calories for all swellables, and is about 390 calories for cellulose. Freundlich also gives a table of values of first heats of swelling.[114] The heat of swelling falls off considerably as the water content of the gel rises. A diagram shows this effect at the end of the section.

Volume changes occur in the swelling process. Generally the volumes are additive, but there is always a slight contraction. Katz[115] gives values for the 'first swelling contraction,' the analogous differential coefficient to the 'first heat of swelling.' This is the volume contraction in cc. of the combined volumes of gel and liquid when 1 gram of liquid is taken up by a very large amount of dry gel. It is 0.29 cc. for casein and 0.26 cc. for artificial starch. Its value is probably similar for cellulose, but accurate determinations are impossible. The ratio of $\left(\frac{dc}{di}\right)_{i=o}$ to $\left(\frac{dW}{di}\right)_{i=o}$ seems to be of the same order for all swellable gels.

The general energy relationships during the swelling of elastic gels are very anomalous. If the swelling be conducted isothermally there may be an almost complete conversion of the heat of swelling into external work. Katz shows that swellable substances, in taking up water, behave like the ideal concentrated solutions of Nernst. A comparison with concentrated solutions of H_2SO_4 and H_3PO_4 would be appropriate.

The energy relationships of dilute solutions are quite different. In the latter case the energy is kinetic and gives rise to osmotic pressure. In the case of the former the energy is due to the molecular attraction between the gel (or solute) and the liquid. Herzog and Weissenberg[116] deal with this aspect of the matter in a recent paper. The discrepancy between the directly measured swelling pressure and that calculated from Katz's formula has been fully discussed by Terzaghi[117] in a recent paper. He quotes Harkins as suggesting that the pressure in the liquid film may be as high as 20,000 atmospheres. Bancroft[96] suggests that the water equilibrium may be altered in the adsorbed film, so that monohydrol alone is present, whereas polyhydrol forms the bulk of liquid water. In this way a condensed water film might serve as a binding cement between the fibres, for the monohydrol would be orientated on the fibre, and the latter has hydroxyl groups of both basic and acid function. At any rate the observations of Katz, to the effect that the first heat of swelling and the first volume contraction of all colloids swellable in water are fairly similar, and that the ratio between these quantities is fairly constant, suggests that the mechanism of swelling and hydration is the same in all cases.

6. The latter relationship also suggests that the total volume contraction of the system would serve as a true measure of hydration. Unfortunately this is very difficult to measure for a porous gel like the

cellulose fibre with a free air-space of nearly 25% It can be deduced by Le Chatelier's principle that increase of total pressure on the gel-liquid system should increase the degree of swelling, and also that increase of temperature should diminish swelling. An important and suggestive paper by Strachan[36] goes pretty completely into the matter, as far as the beating problem is concerned. Strachan uses blocks of vulcanised fibre, as a sort of enlarged model of the papermaking fibre, and measures the imbibition phenomena. In spite of the fact that the vulcanised fibre has undergone a treatment with zinc chloride solution, the analogy seems to be perfectly valid. The vulcanised fibre, if not of too high density, will have an air space similar to that of unbeaten fibre, and the imbibition phenomena can be studied in a leisurely and convenient manner. The removal of entrained air from the fibres must certainly play a considerable part in the beating operation. Strachan finds that pressure accelerates imbibition, and that raising the temperature decreases the final imbibition. The effect of pressure is again shown by Strachan in the hydration which seems to take place on calendering water finish papers. Excessive pressure at a thick spot on the web will give a transparent brittle spot of hardened paper, which is similar in character to what would have been obtained with very wet beaten pulp. The action is highly important in the finishing of certain types of paper. When dealing with the case of temperature, it is not probable that

this will have much effect in the course of beating, at least for moderate variations of temperature, as the effect of boiling wet-beaten stock in water and cooling has already been discussed. Strachan believes that water of imbibition or hydration can be measured by subjecting the fibres to high pressure and measuring the residual water content. He recommends a standard pressure at least greater than 10 lbs per square inch. Nakano[118] has tried this, and concludes that the differences between beaten and unbeaten pulps are too small for the method to be of any value. It is not forgotten that Schwalbe[61] has used a similar centrifuging method to determine the beating degree of pulp. The author deals with this matter in the experimental part of this paper, and fails to detect any considerable differences between unbeaten and very wet-beaten stuff, when using pressures up to 200 lbs. per square inch. In these experiments the pulp cakes were carefully pressed to an equilibrium state. The unbeaten cakes reached this state very much more quickly than the wet-beaten cakes. Strachan believes that the hydration taking place during the beating process is merely an extension of the imbibition taking place on steeping the unbeaten fibre, an extension which is rendered possible by the great increase of specific surface during beating. This imbibition in the vulcanised fibre Strachan proves to occur, according to the velocity law of a unimolecular reaction. (He uses a formula by Reinke.) It is suggestive that Hofmeister used a similar formula for the

swelling of gelatine, and that Kanamaru has applied it to the change in electrokinetic potential during beating. In view of the very slight change in the imbibition water after beating as measured by Strachan's method, it is very difficult to see how the enormous alteration in sheet properties can be accounted for.

7. The phenomena are much more complex for swelling in aqueous solutions. The solute may or may not be adsorbed. Freundlich thinks that a positively adsorbed substance favours swelling, while a negatively adsorbed substance hinders it. Herzog thinks that negative adsorption (preferential adsorption of water rather than solute) necessitates a semi-permeable membrane, but Freundlich thinks this is not so with strongly lyophilic gels.

Much work has been done on the swelling of gelatine and collagen in salt solutions. Procter and Wilson[119] believe that gelatine forms feebly ionised salts with acids and bases, and that the swelling equilibrium is governed by the Donnan semi-permeable membrane equations, postulating an equality of the products of ionic concentration of any two pairs of oppositely charged diffusible ions on opposite sides of the membrane. Loeb[120] works on this basis also, and is particularly careful of the pH value of the solution, both outside and within the membrane. He denies the influence of the lyotrope series of salts on swelling equilibria. Later workers do not agree with Loeb and have re-established the validity of the lyotrope series effect[121]. This is

reasonable enough, as according to the conception of Freundlich, the lyotrope series is an arrangement of ions in order of their hydration capacities. Briggs[122] establishes the connection between lyotrope series effect and ionic mobilities, which latter are again conditioned by the hydration envelope. Bancroft[96] interprets the lyotrope series in terms of a shift in the water equilibrium, caused by the different ions. Different investigators arrange the neutral salts slightly differently in the lyotrope series. Perhaps the most usual arrangement is as follows:-

Anions Cit. > Tart. > SO_4 > Acet. > Cl. > NO_3 > Br. > I > CNS.

Cations Cs > Rb > Na > K > Li > NH_4

The ions at the start repress and those at the end favour swelling of gelatine. It is probably the case therefore, that if a change, such as the swelling of cellulose in neutral salt solutions, shows the lyotrope series effect, it is probably definitely connected with a hydration phenomenon.

The analogy with the behaviour of gelatine must not be carried too far. Bancroft[123] as the result of experiments on dry gelatine, using HCl and NH_3 gases, denies the formation of definite compounds. In solution the case is probably different, and most investigators agree that some kind of salt formation takes place, even although the gelatine itself is not now regarded as a single individual substance.[124] The distinction between swelling due to osmotic action and salt formation, and that due to hydration is therefore of importance.

The first is an osmotic phenomenon, and the second follows the conceptions of Katz. The first should be favoured by rise of temperature and the second depressed. Theis[125] and his coworkers have shown the distinction in a very practical manner. Both Procter and Loeb ascribe swelling at the isoelectric point to a kind of solid solution. Katz points out the disparity between the sizes of the molecules of gel and water, and accounts for the volume contraction by the intrusion of water molecules between the loosely aggregated gel molecules. Thus the total volume contraction of the system is the central feature of a swelling which is due to hydration. Theis and his coworkers adopt this idea, and show that the total volume contraction is a maximum at the isoelectric point for gelatine, although the swelling shows maxima at some distance on either side, when both swelling and total contraction are plotted against pH value. They also show that total contraction diminishes with rise in temperature, although swelling due to salt formation, being an osmotic phenomenon, should increase. Thus salt-formation swelling may eventually lead to peptisation at higher temperatures, but there ceases to be any necessary connection between hydration and peptisation. The methods of measurement were either a simple dilatometer or a series of density measurements. An interesting group of curves was obtained of which a few are here reproduced (end of section) along with a curve by Morgan and Libby[89] on the variation of beating degree with pH value in the case of cotton and sulphite

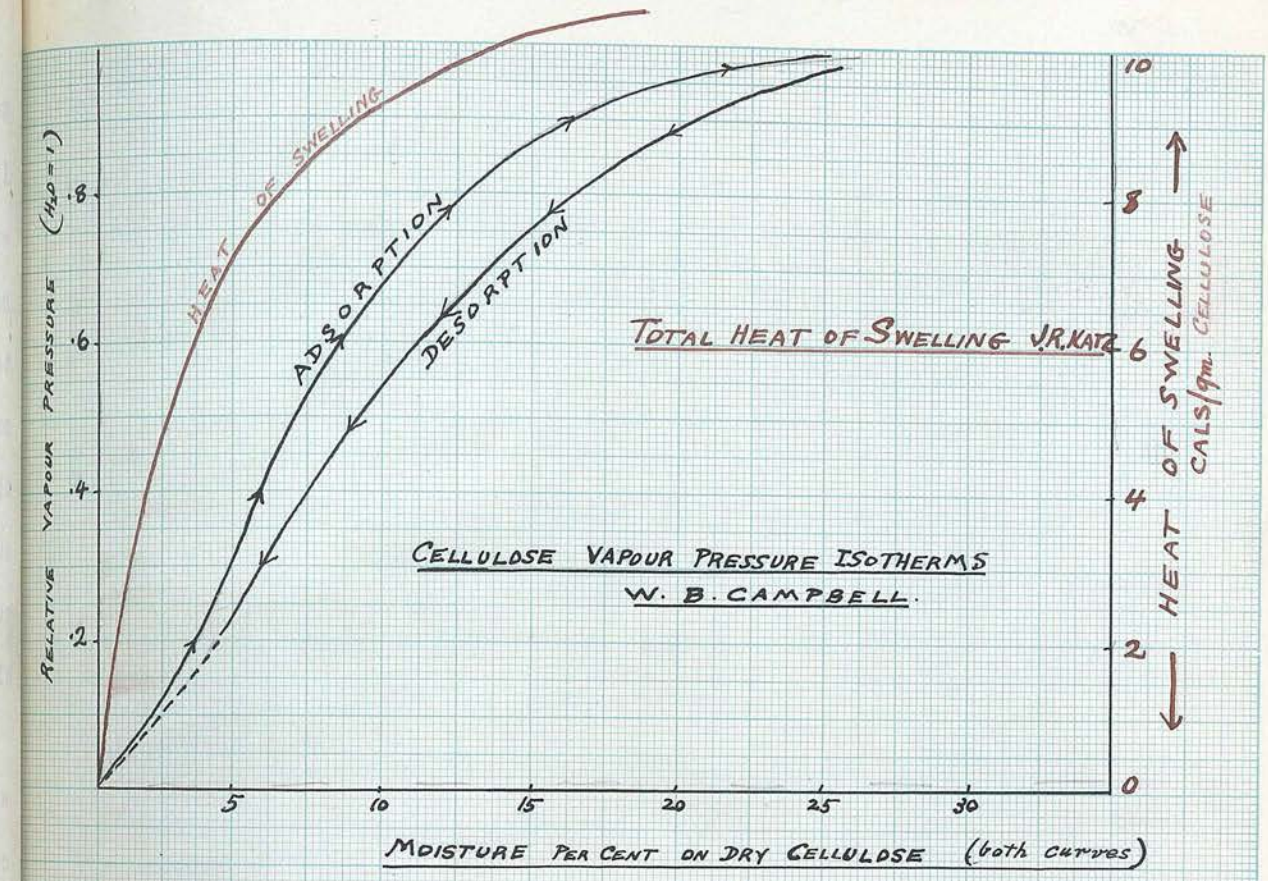
wood fibres. It is unlikely therefore that von Weimarn's methods for the peptisation of cellulose in concentrated salt solutions have any analogies amongst the phenomena of beating. Except where noteworthy degradation occurs, we have no adequate or reliable data as to the effect of dilute solutions of acids, bases or neutral salts on beating.

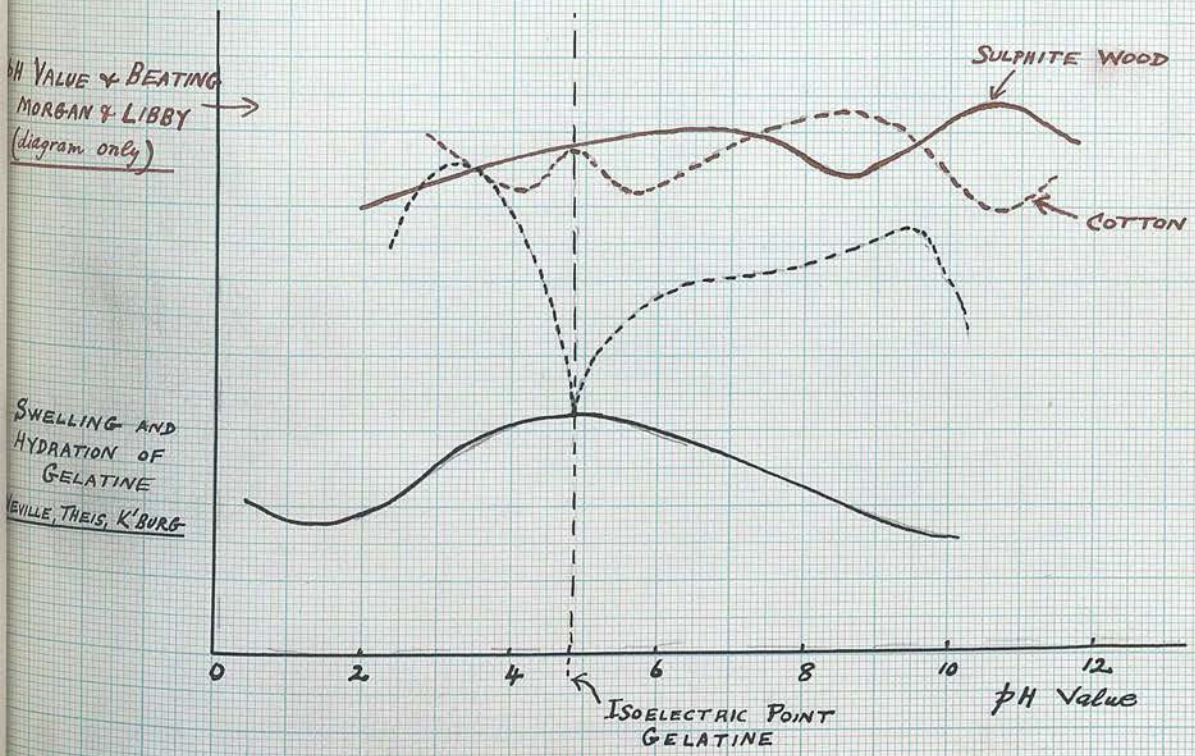
8. The question of 'free' and 'bound' water in colloids has been very much discussed of recent years, especially in connection with biological phenomena. The paper by A. Kuhn[107] has already been noticed. Recent work has been largely described by R.A. Gortner[126] and his associates. D.R. Briggs[127] reviews the experimental methods. 'Bound water' is to be defined as osmotically inactive water for the solution of such solutes as sucrose, or again as water which cannot be frozen out by prolonged exposure to such low temperatures as -20°C. Newton and Gortner measured the 'bound' water by determining the freezing point depression produced by the addition of a definite amount of sucrose to a solution, of which the total water content had been determined in another manner. A.V. Hill used a similar method, but observed the lowering of vapour pressure of the solution. The freezing out methods were developed by Rubner and Thoenes, and although they measured the ice formation calorimetrically it has also been done by means of a dilatometer. It appears that definite results can be obtained for 'bound' water in individual cases, but that the values obtained by different methods do not always agree among themselves. The bound water of gelatine

gels seems to vary according to the dilution of the gel[126 i]. It cannot be argued that 'bound' water is a well defined entity. This is quite to be expected, for Nutting[128] has found the adsorptive layer of water on silica gel to be as much as 100 mols. thick. In such a case the orientation of the water dipoles would be complete and the solvent properties of the water nil at the silica surface, whilst the orientation would decrease and the solvent action would increase gradually towards the outside of the adsorption layer.

The freezing out method does not seem to have been applied to the determination of 'bound' water in beaten cellulose. G.H. McGregor[129] has used the freezing point depression method with sucrose as the solute and he finds that there is no evidence of the presence of 'bound'water. The author will describe some work on the same lines in the experimental part of this paper.

To conclude, it must be pointed out that the phenomena of wetting, adsorption and swelling are hardly distinguishable from each other in many cases. Some inelastic gels show considerable heats of wetting with no change of volume. Some gels with positive heats of swelling only swell readily at high temperatures (starch in boiling water). Again some substances, which at high concentrations dehydrate the lyophilic colloids, (alcohol, glycol) may promote swelling and hydration at much lower concentrations.


HEAT OF SWELLING
ADSORPTION
DESORPTION
RELATIVE VAPOUR PRESSURE (H₂O = 1)
.2
.4
.6
.8
TOTAL HEAT OF SWELLING J.R. KATZ
CELLULOSE VAPOUR PRESSURE ISOTHERMS
W. B. CAMPBELL.
HEAT OF SWELLING CALS/gm. CELLULOSE
0
2
4
6
8
10
5
10
15
20
25
30
MOISTURE PER CENT ON DRY CELLULOSE (both curves)


SH VALUE & BEATING
MORGAN & LIBBY
(diagram only)
SWELLING AND HYDRATION OF GELATINE
EVILLE, THEIS, K'BURG
SULPHITE WOOD
COTTON
0
2
4
6
8
10
12
ISOELECTRIC POINT GELATINE
pH Value

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VII.

BEATING AND SHEET PROPERTIES.

1. The mechanical treatment of pulp in the beater must achieve its purpose in the properties of the sheet of paper produced. The change in these properties may therefore serve to some extent as a means of investigating the changes undergone by the pulp during the beating process. The relation will not be one which is direct and simplex, as the beating changes are many and the mechanical characteristics of a sheet of paper are not simplex either. A group of general and approximate predictions may be laid down however as follows:-

(a) The separation of the fibres from each other during beating will help to give orientation, uniformity and some degree of strength to the sheet.

(b) The reduction of the fibres by cutting and fibrillation will delay drainage on the papermachine wire, and the size of reduction will aid the felting process both on the wire and at the presses. Thus the uniformity and 'look-through' will be improved, and air and liquid porosity will be diminished. Fibrillation should greatly improve sheet strength whilst preserving the natural stretch of the sheet under mechanical stress.

(c) The formation of a colloidal or hydrated surface film on the fibres may delay drainage on the wire to some extent, will undoubtedly assist cohesion of the fibres at the presses and on the drying cylinders, and will increase tensile and bursting strength. There

will be undesirable effects however as regards shrinkage on drying, cockling on change of humidity and loss of stretch. Hydration* will close the sheet and decrease porosity to air and liquids. The surface will be improved, although this may be achieved as well by the addition of fillers, and transparency will be increased.

(d) Excessive beating will probably continue to increase hydration, but the additional fibre reduction will reduce the strength qualities of the sheet, and the undesirable hydration effects will be predominant. Nothing is known as to the effect of beating or steeping on the strength of the individual fibre. The effects cannot be isolated.

The above analysis while it may be generally correct in outline, is subject to certain qualifications in practice. Thus Harrison(130) in a recent paper on the beating of wood pulp comes to the conclusion that fibrillation in this case only develops to any degree after the maximum strength has already been attained. In such a case the increase of beaten strength would be almost entirely due to the colloidal surface film. The case will be vastly different for rag fibres, where hydration is slow and fibrillation has time to develop. In any case the ideal of the papermaker, as of the artificial silk maker, is to obtain the final product with minimum fibre damage in the course of manufacture, and maximum utilisation of the natural properties of strength and elasticity.

2. An enormous amount of work has been done in recent

* 'HYDRATION' = Colloidal surface film development (see p. 70 note)

years in different countries on practical laboratory methods for determining the strength and beating characteristics of paper pulps. In Britain the results have been made available by the Pulp Evaluation Committee of the Technical Section of the Papermakers' Association[131] The interim report gives a complete historical review of the subject and a bibliography. In America and Germany similar work has been done.

The question of a standard laboratory beating appliance is still undecided. It is pretty generally agreed that a model beater or refiner is unsuitable for research work. The claims of the Abbé pebble mill and the Lampén[132] single-ball mill are much discussed. The present author has used the pebble mill, although it is probable that the Lampén mill may give more reproducible results. The pebble mill, for research purposes, allows of far greater scope in varying the severity of the beating treatment.

The Pulp Evaluation Committee report describes the sheet making process minutely. The foundation of the method is of course the Wilén sheet machine, and the work done by E.P. Cameron on the technique of model sheet making in Canada. In the Laboratory of Messrs. Tullis Russell & Co., Ltd., the method adopted has been different in some respects, and a technique has been in operation for several years which is well described in a recent paper by MacDonald and Cramond.[133] This method has been substantially adopted in such parts of this experimental investigation, as have involved the

study of sheet properties as a result of graded beating. Briefly the method is as follows:-

The beaten (or unbeaten) pulp is disintegrated in a very dilute condition for 10 minutes in the disintegrating churn. Sheets of a standard substance of 100 gms. per sq. M. are made on a Wilén sheet machine, which gives 8 inches square sheets. The sheets are couched successively between felt and blotting papers, the sheet being couched on to a stainless steel plate. The final couch pressure is 200 lbs. per sq. inch and is applied for 2 minutes. Drying is conducted on a drying cylinder, electrically heated to 100°C, for 10 minutes. Free shrinkage cannot take place on drying. The sheets are conditioned to a relative humidity of 65% before testing.

3. There is a good deal of literature on the testing of paper. An excellent review is given in 'Paper Testing Methods' issued by T.A.P.P.I. (U.S.A.) in 1929. The influence of variation of relative humidity on the various properties is described. There are also quite a number of papers published in Britain.(134) The bulk and air-porosity tests are an indication of closeness of texture, but each is subject to considerable experimental error. Bulk depends greatly on pressure, and air-porosity is subject to considerable variations, even with well made hand-sheets. As an indication of beating strength characteristics the 'burst' and 'tear' tests are the most satisfactory, but their results must be studied together. The 'tear'test is especially sensitive to reduction in fibre length, and should be noted

as an indication of excessive reduction of the fibres if it is low and is associated with a high 'burst' test. The 'burst' is considerably raised by hydration up to a fairly advanced stage of the beating process, and is very little affected by the loss of the stretch properties of the fibres. Accordingly the author has usually judged the results of the beating process by the associated 'burst' and 'tear' tests on the beaten sheets. The question of humidity control must again be emphasised, for the 'tear' and 'burst' are affected in opposite directions by deviations from the standard of humidity. Again it is unlikely that the same law of variation will hold for very wet beaten and practically unbeaten pulps. The tensile strength is admitted to be a less complicated mechanical property than the bursting strength, but considerations of simplicity and rapidity of determinations, and reduction of the possibility of error by small areas of weakness in the handmade sheets, have restricted the author to the two tests already named. The Ashcroft bursting tester has a very small area of puncture, and the look-through of the sheet enables one to select a sufficient number of uniform places for testing. The Elmendorf tear tester measures the energy absorbed in a tear of definite length, the tear having been already started. Thus the test is an integrating test, and is not liable to be vitiated by local weaknesses in the sheet. The tensile strength at zero length, as a measure of individual fibre strength, has not been used.

4. It is noteworthy that some of the effects believed

to be peculiarly attributable to the beating operation can be reproduced by pressure on the moist sheet. The question has been recently examined by R.H. Doughty.[135] He has used a large range of couching pressures on model sheets, pressures varying from 2 to 300,000 lbs. per square inch. The experimental conditions did not usually allow of the highest pressures being used. He states his results in the form of a relationship between sheet strength and 'solid fraction,' the latter being the volume percentage of cellulose of density 1.5 in the finished sheet. For unbeaten pulp the strength seems to vary as the square of the 'solid fraction,' and with high pressures the effects of beating are simulated on the unbeaten pulp. This is apparently a case of reducing the distance between the cellulose micelles and thus making the residual valencies active without the intermediary of the colloidal surface film produced by beating. This work is thus additional evidence in favour of the colloidal surface film theory of hydration.

Even when beating and sheet making are conducted under optimum conditions the final sheetstrength is very much below what has been calculated to be possible from theoretical principles. Mark[136] has calculated the ultimate tensile strength of cellulose fibres with ideal orientation, by considering the energy required to rupture the main and secondary valency bonds of the molecule respectively. For a rupture of the primary valency bonds he finds the tensile strength should be 800 Kg. per sq. mm., for the secondary bonds 200 Kg.

per sq. mm. Generally this would give from 3 to 4 x 10^5 lbs./sq.". The value would be decreased to one third of this for random orientation, and 100,000 lbs. per sq. inch gives a breaking length of 47,000 metres, which is about three times as great as is found for the strongest papers in the machine direction. It is clear therefore that the potential valencies are never fully utilised in the manufacture of paper.

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E X P E R I M E N T A L.

VIII

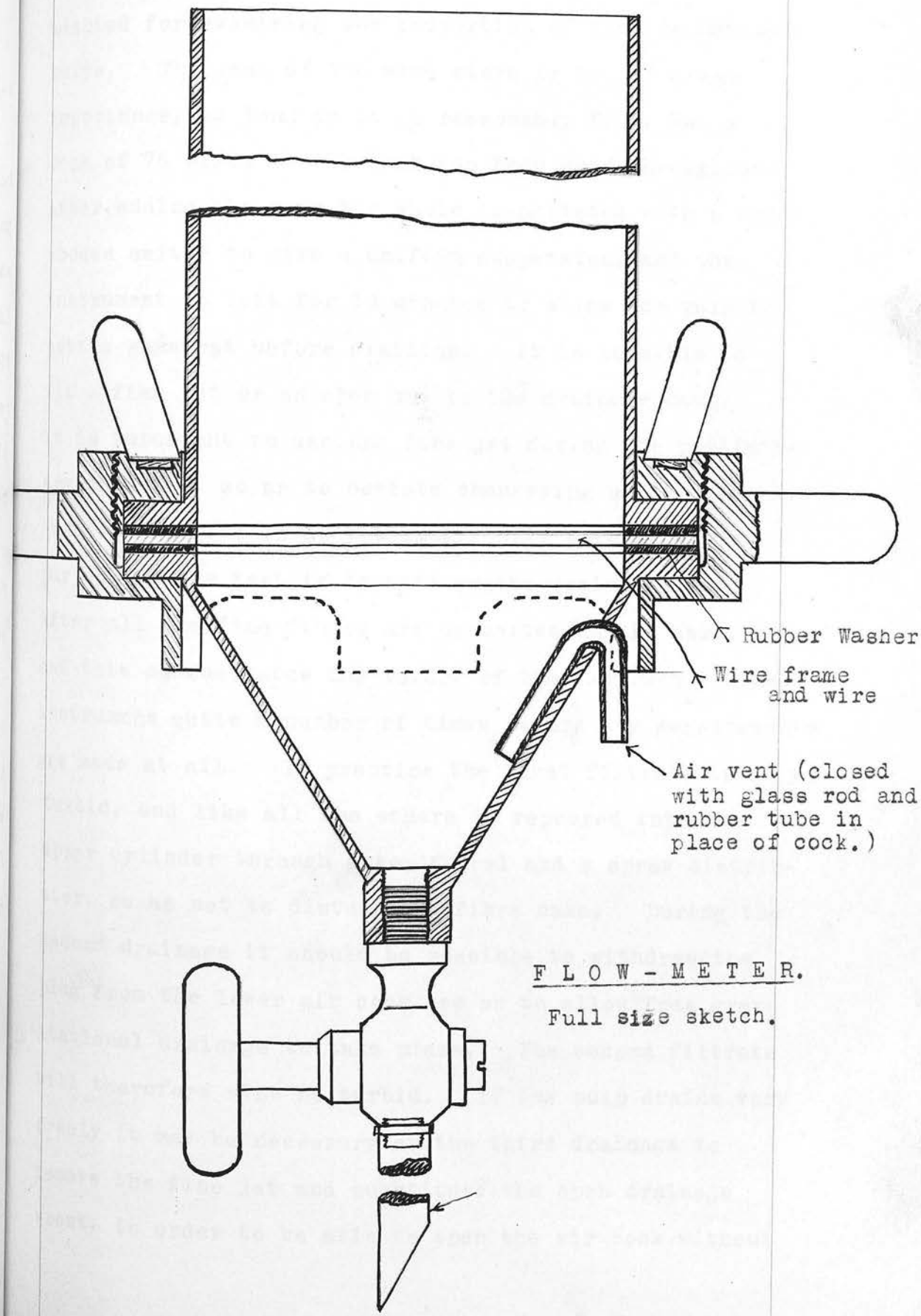
THE DRAINAGE PROPERTIES OF SUSPENSIONS OF BEATEN FIBRES.

(1) Apparatus & Method.

The development of practical 'freeness' testers has been briefly dealt with in section V, p. 49 of this paper. The main objections to the usual freeness tester as a research instrument were found to be its comparative lack of sensitiveness to the effect of the finer fibres, fibrillae and fibre debris, and the impossibility of correlating the 'freeness' or 'wetness' values by a linear law with the weight of fibre used, and the viscosity and density of the liquid medium of suspension.

These defects have been overcome in a fairly satisfactory manner by the instrument shown diagrammatically on the next page. For convenience the instrument will simply be referred to as a pulp flow-meter, and the resulting descriptive number for any pulp will be referred to as the flow-constant. As the instrument can be used with other liquids than water a convenient notation for flow constants will be F_{aq}, $F_{alc.}$ respectively for the constants determined in water, alcohol and so on.

The Flow-meter is similar in design to the old Schopper type of freeness tester. The aircock below the wire and the drainage cock are closed while sufficient distilled water is poured in from above to cover the wire adequately. For this purpose 150 cc. is more than enough, but it is usual to use 250 cc., and then to add the desired quantity of beaten pulp, previously disintegrated by shaking with glass beads or in some other



F L O W - M E T E R.

Full size sketch.

manner, suspended in exactly 350 cc. of water. It should be observed that the instrument is not well adapted for examining the properties of free or unbeaten pulps. The mesh of the wire sieve is not of great importance, so long as it is reasonably fine, but a mesh of 76 wires to the inch has been used throughout. After adding the pulp the whole is agitated with a small wooden switch to give a uniform suspension, and the instrument is left for 10 minutes to allow the pulp to settle somewhat before draining. It is possible to fit a fine jet or an open one to the drainage cock. It is important to use the fine jet during the preliminary draining, so as to obviate channeling while the fibre cake on the wire is as yet imperfectly formed. The purpose of the test is to measure the drainage-rate after all the fine fibres are deposited on the cake, and this necessitates the return of the filtrate to the instrument quite a number of times before any measurements are made at all. In practice the first filtrate is very turbid, and like all the others is repoured into the upper cylinder through a tap funnel and a spray distributor, so as not to disturb the fibre cake. During the second drainage it should be possible to withdraw the plug from the lower air cock, so as to allow free gravitational drainage to take place. The second filtrate will therefore also be turbid. If the pulp drains very freely it may be necessary at the third drainage to remove the fine jet and substitute the open drainage spout, in order to be able to open the air cock without

danger of water coming out instead of air being sucked in. Usually the instrument has been used to examine well beaten pulps, and this procedure is then unnecessary. In such a case however the fine fibres settle very slowly, and the standard method is to filter off 5 successive portions of 250 cc. each before measuring the time of drainage of the 6th. portion. It is still not certain that all the fibre is in the cake. As can be shown from the theory of the operation, a guide can be obtained by observing the ratio of the drainage time for 100 cc. and 250 cc. respectively. If the time is measured by closing the drainage cock and repouring the small amount of drainage water, so that the flow commences with exactly 600 cc. in the cylinder, there should be a constant ratio between the flow times for 250 cc. and 100 cc. respectively, after the cake is completely formed. This ratio will increase if fine fibre continues to deposit itself on the cake and slow the drainage rate. Its normal value is 2.95 - 3.00. The flow times for 250 cc. continue to be measured for the 7th. and 8th. drainage portions, and also the temperature, and if necessary the viscosity-density ratio of the liquid. It is clear that the dry weight of pulp used for a test can be determined either from the residual cake, by couching off the wire on to filter or blotting paper and subsequent drying at 100°C., or from a portion of the original suspension by draining through a filter paper on a Buchner funnel. There is no difficulty in separating pulp cake and filter paper. Measurements

can also be made of the weight of water retained by the pulp after equilibrium drainage, but this varies little for beaten and unbeaten pulps. The weight of pulp used can be varied so as to give a suitable flow rate, neither too slow nor too fast, and it will be shown that within certain limits the flow-time is proportional to the weight of dry fibre in the cake.

The flow-constant is defined as the quotient of the flow-time for 250 cc. of water under steady-state conditions and at 20.2°C., by the dry weight of pulp used. The choice of 20.2°C. is in order to get an easy temperature correction for the viscosity of water at different temperatures. The density correction for water temperature is within the limits of experimental error and is neglected. (Viscosity of water at 20.2°C. = 0.01 C.G.S. units). If the flow is considered to be in accordance with Poiseuille's law, the experimental method is seen to be quite justified, even if that law must be modified by electro-osmosis effects.

Poiseuille's equation for the flow of liquid through a capillary tube is as follows:-

$$V = \frac{\pi P r^4 T}{8 \eta l}$$

(P = hydrostatic pressure causing the flow.
(V = Volume of liquid delivered in time T.
(η = viscosity of liquid.
(r = radius of capillary.
(l = length of capillary.

In the present case the capillary dimensions and the viscosity are constant during the determination, but the pressure varies. The pressure is proportional to the volume of water in the cylinder, less that

quantity which may be held to saturate the cake without increasing the hydrostatic head.

Hence $\frac{dV}{dT} = k(c - V)$ k,c being constants.

Integrating, $\log(c - V) = c_1 - kT$

But when $V = o$ $T = o$ Hence $T = \frac{1}{k} \log \frac{c}{c - V}$

If p = the volume of water inoperative to produce hydrostatic pressure it will vary from a small quantity up to 20 cc. or more. Then for 250 cc. volume delivery from starting conditions -

$$T_{250} = \frac{1}{k} \log \frac{600 - p}{350 - p}$$

Likewise $$T_{100} = \frac{1}{k} \log \frac{600 - p}{500 - p}$$

Hence $$\frac{T_{250}}{T_{100}} = 2.96 \ (p = o) \text{ or } 2.98 \ (p = 20)$$

In practice the ratio found is always from 2.95 to 3.05 under equilibrium conditions. If it can also be shown that T_{250} is directly proportional to the weight of dry fibre used, and directly proportional to the viscosity-density ratio of the suspension liquid, the flow constant can be taken as a quantity which is characteristic of the average capillary radius of the wet fibrous cake. This is probable, as the length of the capillaries is less likely to change than the the radius in ionic coagulation and dehydration experiments, and also because the capillary radius occurs in the flow equation raised to the 4th. power. A considerable number of experiments, and modifications of the apparatus were made before anything like satisfactorily reproducible results were obtained. The fibrous material was always the same, viz. easy

bleaching sulphite wood pulp. In all the early experiments the beating effect was produced in a small porcelain edge-runner mill. In the experiments subsequent to 1926 a ball mill was used. The pulp was bleached in the laboratory under standard conditions. Distilled water was necessary in all experiments. The preparation and purity of the pulp will be described in a subsequent section dealing with volume-contraction on drying.* It is unnecessary to deal with the matter twice as the procedure was always the same. The flow meter was of brass, nickel-plated and the wire of phosphor-bronze.

(2) Standardisation, Accuracy of Results.

(a) Uniform Flow Conditions.

Much depends on the pulp which is being examined whether steady-state conditions can be reached in the 6th. or even the 8th. flow period of 250 cc. An extremely well beaten pulp when tested in pure distilled water contains a portion of fibre debris very difficult to settle, and which even after apparently complete settling, continues to compact itself on to the cake and may give a ratio of 8th. to 7th. flow time much greater than 1.05. Such a pulp if coagulated or flocculated to some extent, with even a small trace of an electrolyte, will behave quite normally, the corresponding ratio falling to 1.01 - 1.03. Similarly the T_{250}/T_{100} ratio will be abnormally high for such a pulp (say 3.15 instead of 2.95). There is no real cure for such a state of affairs, because if the repouring process is continued up to the 10th or 12th. time, the

* Part IX,2

cake will continue to compact itself, and the results will not be accurately comparable with those obtained for the same pulp with the addition of electrolytes. Therefore a uniform practice has been followed - to correct the 8th. flow time for 250 cc. by adding to it the difference between the 7th. and 8th. times.

It is of the greatest importance that the initial drainage of the cake should not be too fast. Hence very fine jets are used. These jets will deliver the contents of a 50 cc. pipette with a 6" stem below the bulb in a period of over 25 seconds, there being of course a wide orifice on the lower end of the stem of the pipette.

(b) Correlation of Flow Time with Dry Weight of Cake.

No of Tests Done.	Dry Weight.	$\frac{T_{250}}{T_{100}}$	Cor. T_{250}	T_{250} Deviation.	$F_{aq.}$	$\frac{WET}{DRY}$
2	1.29	3.00	7.19		5.58	18.0
3	1.47	3.07	7.50		5.11	18.0
3	1.91	3.09	9.79	0.22	5.12	18.0
3	1.94	2.99	10.03	0.37	5.17	18.3
3	2.28	3.09	12.40	0.34	5.44	18.5
6	2.88	3.00	14.91	o.30	5.18	17.8
3	3.97	2.95	13.67	0.89	3.44	18.0
2	5.95	2.97	20.86	1.94	3.50	16.1
Mean		3.02			5.27	17.8

The above results were obtained on a pulp which was kollerganged for about 4 hours in the model edge runner.

It is a moderately free pulp. At this date (1925) a Schopper Riegler freeness tester was not yet available to me. The table pretty well explains itself. The 'Deviation' column refers to the average deviation in each set of experiments from the average value of T_{250} corrected for temperature. The accuracy of a set of experiments run side by side from identical batches of diluted pulp can be judged from this. Deviations should not exceed 4% from the mean value. The value of $F_{aq.}$ is got by dividing T_{250} by dry weight of pulp used. The last column gives the ratio of the wet weight of the final pulp cake drained to equilibrium, divided by the dry weight. It is quoted here, as I have found it to be sensibly constant for a wide range of beating degree. It is therefore useless as a criterion of beating degree. The mean value of F_{aq} in the last row is arrived at by discarding the abnormally low values of the last two experiments. It is quite clear therefore that F_{aq} is only constant over a mean range of dry weights for pulp cakes. In this case F_{aq} comes out too high if the pulp dry-weight is reduced to 0.8 gms. In cases of very well beaten pulps one can use dry weights down to 0.1 gm., but in such cases the flow time is prohibitively long for such weights as 1.0 gm. The independence of F_{aq} on pulp weight used has also been proved for mean ranges of very wet beaten pulps. The tables are not included here. The independence is one of degree only, and the only safe experimental rule is to keep the conditions of comparative experiments as near as possible to each

other. The following measurements were made (Jan. 1926) on a pulp Bj which had been kollerganged to a much higher degree:-

Dry wt.	0.200	0.247	0.298	0.400	0.488
F_{aq}	117.8	127.4	132.6	122.5	130.6

For this pulp the ratio $\frac{\text{Wet}}{\text{Dry}}$ weight had risen to 22.0.

(C) Temperature Effect.

In the last example quoted the temperatures during some of the different experiments varied from 12.6°C. to 18.6°C. In every case T_{250} was corrected for the variation in the viscosity of water. A table was constructed interpolating correction percentages to be subtracted from the observed flow time for intervals of 0.1°C. The standard temperature chosen was 20.2°C. when η = .01 absolute units for water.

Three further groups of experiments were performed (24/2/26) at average temperatures of 12°C., 16.5°C., 24.2°C. on a wet beaten pulp, and the flow times were corrected to 20.2°C. by the extension of the same table. The results given below show that between 10°C. and 25°C. the flow is inversely proportional to the viscosity of the water used.

Dry wt.	Av. °C.	Uncorrected T_{250}	Devn.	Corrected F_{aq}
.242	11.9	45.76	.97	152.4
.243	16.5	39.87	1.77	149.5
.240	24.2	32.54	.94	147.7

At each temperature 3 experiments were done, and the dry weights were all about the same. The variation in the density of water is only about 0.3% over the

range 10°C. to 25°C. and does not affect the experiments. The above variations are within the region of experimental error and cannot be held to show any dehydration phenomena.

(d) Constancy of F_{aq} with time.

An extended investigation of ionic or other influences on the flow constant of a pulp may take many days, especially if the work has to be carried out in spare time and at odd periods of leisure in an industrial laboratory. It is of importance to know whether F_{aq} alters on prolonged storage or on steeping of the wet beaten pulp. Unfortunately this is the case, and the alteration, although invariably an increase, is by no means constant. In many cases it was found to be practicable to preserve the beaten pulp in a moist state for 1 or 2 months before using it. After that period the variation on further storage was found to be negligible.

As an instance of what occurs, the case of a pulp used for investigating the ionic coagulation effect may be cited. The pulp had been already stored in the wet and beaten condition for a week, yet its flow constant increased from 51.5 to 56.6 in the course of the next 50 days. In another case, which was specially investigated from this point of view, a very much greater increase was found, the value of F_{aq} nearly doubling itself in two months' time. In yet another experiment a trace of phenol was added to ensure sterilisation, and a lesser increase was found. This does not indicate

that the change proceeds in general from bacterial action, as complete stabilisation can usually be effected by adding an inorganic salt in very low concentration, e.g. NaCl $\frac{M}{1000}$ $Al_2(SO_4)_3$ $\frac{M}{10,000}$. It is probably a phenomenon related to electrokinetic potential.

(e) Viscosity Effect in other Liquids.

Before the experiments at temperatures up to 25°C. were performed, the effect of varying the viscosity of the suspension liquid was tried out on several aqueous solutions, including solutions of common salt, sucrose, glycerin and ethyl alcohol. The results were unsatisfactory in every case, and it was concluded that phenomena of hydration exerted a considerable influence. The viscosities of the clear filtrates were determined at the same temperature as prevailed at the end of the drainage test, by means of an Ostwald viscometer which had a flow period for water at 20°C. of 58 seconds. As the correction factor should be the viscosity/density ratio, the relative flow periods in the viscometer were used directly as correction factors. The results were as follows:-

	No. of Expts.	Flow Viscometer	Corrected Flow Const. Average.
Water Experiments	10	58 secs. (20°C)	16.1
Sucrose 20% Soln.	3	125 " "	30.0
" 10% "	4	82.6" "	26.1
NaCl Soln. 38°Tw	4	94.9" "	9.05

	No. of Expts.	Flow Viscometer	Corrected Flow Const. Average.
Glycerin Soln. 13° Tw	4	132 secs. (20°C)	11.43
" " 5½° Tw	4	81.6 " "	16.33
Alcohol 39% by wt.	4	171 " "	8.84
" 95% " "	4	116.7 " "	2.52

Notes.

(i) All the dry weights of pulp used were in the neighbourhood of 1 gm. Hence it will be seen that the sucrose experiments were not too satisfactory as T_{250} became as large as 64 mins. and no doubt a certain undue compacting of the cake took place. For 95% alcohol T_{250} was only 5 mins.

(ii) The sucrose solution was made up 20% and 10% respectively by weight, the alcohol similarly, while the salt and glycerin solutions were recorded on a density basis using the Twaddell hydrometer.

(iii) The salt solution effect will be seen to fall into its place later amongst the ionic coagulation phenomena. The alcohol and glycerin effects are undoubtedly due to some dehydration process, and the alcohol effect will be studied in detail later on.

(iv) The curious result with sucrose seemed to have no satisfactory explanation. It was deemed advisable to repeat the work just before writing the present thesis, with the result given below.

The weights of pulp used were the same when determining

the flow constants in water and in a 10% solution of pure sucrose. The flow times being corrected for viscosity to the water standard at 20.2°C. the results were -

(F_{aq} = 129.5 (3% deviation from mean of 2 expts.)
($F_{soln.}$ = 151.7 (" " " " " " ")
(An increase of 17% in flow constant.

Dilute solutions of sucrose 2 - 3% showed no change from water.

It may be remarked here that glucose is commonly used to aid the 'wet beating effect' in the beaters in the manufacture of glassine papers, and a glucose solution is used to moisten such papers before calendering.(137)

It has not been found possible to study the matter further, but it is known of course that the sugars are highly hydrated large molecules, which might appreciably obstruct the capillary pores of the fibres if adsorbed to any extent. It must be observed that there is no evidence that the viscosity effect during drainage tests on such thin pulp cakes follows Poiseuille's law with accuracy, where the viscosity differs greatly from that of water.

(3) Coagulation Due to Electrolytes.

A few preliminary experiments were done to see if the addition of electrolytes to the aqueous solution in which the flow test was performed had any material effect on the result. The effect was found to be surprisingly large, the final flow-constant sometimes falling to 50% of its value in pure water. Another set of preliminary tests showed that the effect varied with the concentration

of salt in the solution and with the valency of the cation. Evidence was also obtained of the adsorption of the cation from the solution. It was then deemed necessary to investigate the whole question carefully with the results which are displayed in the tables of the succeeding pages.

The water used was distilled in the laboratory using a block tin condenser. It was not redistilled. It was found that although the pH value of the water was often 5.5 this was due to CO_2 and the pH value rose to 7.4 on boiling and cooling. The pH determinations were all made colorimetrically using the British Drug Houses Ltd. series of sulphon-phthalein indicators and a comparator for values covering the methyl red, Bromocresol purple, Bromo thymol blue and Phenol red ranges, and using a colour chart outside of these ranges. The distilled water was shown to be good by the change in the Phenol Red colour by the addition of a drop of $\frac{N}{50}$ acid or alkali to 100 cc. water. The salts used for the work were usually the British Drug Houses 'analytical reagent' quality or the recrystallised salt.

A few remarks should be made about the method of tabulating results. It is necessary to record the dates of the experiments (year 1926 all) as F_{aq} changes slowly as time progresses. In this case the change was not great but for all experiments prior to 1st. June the value 51.5 was used as a comparative basis; for later experiments the value 56.6 has been used. Perhaps the change is irregular and perhaps the experimental error

accounts for a part of it. The pulp used was always the same, a well kollerganged bleached sulphite pulp Bk. This was kollerganged in the model edge runner for 12 hrs. The ash content was 0.4%. The solutions were all calibrated according to molar concentration. The dry weights were obtained by drying the final cake to constant weight at 105°C. In some cases previous washing with distilled water was given but with dilute solutions this was deemed to be unnecessary, and the assumption was justified by experiment. The temperature of the 8th. or final drainage period was recorded and this figure used to correct all flow times to 20.2°C. according to the water viscosity table. The Flow Constants (F) are thus calculated. The last column shows the percentage fall in (F) in the various cases. Where there is a rise this has been stated.

The period during which the pulp was steeped in the salt solution was from 15 - 20 hours, according to practical convenience. In one case NaCl$\frac{M}{50}$ (a) the test was done at once after mixing and it cannot be said to have affected the result to any extent. In practice then the pulp for an experiment was steeped in 350 cc. of the salt solution, and 250 cc.of the same salt solution was used to cover the wire of the tester.

The possibility of acid solutions dissolving heavy metal ions from the metal tester itself was not lost sight of. Of course the metal of the tester comprised a nickel plated part, a bronze wire and a brass nozzle. No solutions of a very high degree of acidity were used.

There may have been some effect in the case of the H_2SO_4 and HCl. experiments but the final pH value of the solution in that case would mean that the acid solution had become transformed into nickel or copper salt solutions with the possibility that the metallic ions would then be adsorbed by the pulp. Observations on adsorption will be mentioned later, also the univalent ion tests Nos. 36 - 39 where a certain amount of gelatine solution has been added in order to see if protection against coagulation occurs or not.

Reproducibility of results is seen to vary in the different cases. In all cases where the fall in the value of F is at all considerable (20% or more) the results are fairly reproducible, often within 2 or 3% of each other. In those cases where the fall in F is very small, or there is actually a rise, we seem to be in an unstable region where results are not readily repeated with accuracy.

TABLE I. Water and Univalent Cations.

No.	Date	Nature of Soln.	pH Soln.	Dry Wt.	^oC 8R	T_{250}	F	
* 1.	29.4	Water	6.1	.372	17.3	19.67	49.2)	
* 2.	29.4	"	6.1	.227	17.0	13.14	52.6)	51.5
* 3.	19.5	"	6.6	.372	18.3	20.57	52.7)	
4.	23.6	"	6.3	.508	18.7	30.05	57.0)	
5.	23.6	"	6.3	.496	18.6	27.60	53.5)	56.6
6.	26.6	"	6.4	.496	19.1	26.61	52.2)	
7.	5.7	"	6.7	.495	16.0	32.45	59.9)	
8.	5.7	"	6.6	.474	16.1	31.75	60.4)	

Continued p112.

TABLE I. Water and Univalent Cations. (Cont.)

No.	Date	Nature of Soln.	pH Soln.	Dry Wt.	°C 8R	T_{250}	F	Fall %	
* 9.	19.5	NaCl $\frac{M}{50}$ (a)	6.4	.378	18.3	12.18	30.7	40.4	
* 10.	20.5	" (b)	6.3	.375	19.9	11.07	28.9	43.8	
* 11.	20.5	" $\frac{M}{200}$	6.3	.376	19.8	12.31	32.1	37.8	
12.	21.5	" $\frac{M}{500}$	6.3	.385	19.2	15.88	40.3	21.7	
13.	21.5	" $\frac{M}{1000}$	6.3	.374	19.1	16.65	43.3	15.9	
14.	21.5	" $\frac{M}{2500}$	6.3	.369	19.2	18.05	47.8	7.2	
15.	21.5	" $\frac{M}{5000}$	6.3	.370	19.2	20.59	54.3	5.44	rise.
16.	26.5	Na_2SO_4 $\frac{M}{50}$	6.7	.477	20.7	15.20	32.2	37.4	
17.	26.5	" $\frac{M}{200}$	6.7	.495	20.7	15.30	31.3	39.3	
18.	26.5	" $\frac{M}{1000}$	6.7	.488	20.6	19.30	39.9	22.4	
19.	26.5	" $\frac{M}{5000}$	6.7	.489	20.6	24.00	49.6	3.7	
20.	2.7	" $\frac{M}{20,000}$	6.7	.493	17.0	29.43	55.15	2.6	
21.	5.7	" $\frac{M}{100,000}$	6.6	.483	16.1	31.70	59.15	4.5	rise

* Cases where duplicate experiments have been done and average results quoted. Duplication of results quite good.

22.	29.5	NaOH $\frac{M}{50}$	>11	.493	17.8	22.05	42.15	18.2	
23.	29.5	" $\frac{M}{200}$	> 9.3	.497	18.0	22.52	42.9	16.7	
24.	29.5	" $\frac{M}{1000}$	8.9	.498	17.95	23.68	45.0	12.7	
25.	29.5	" $\frac{M}{5000}$	7.4	.499	18.0	26.6	50.5	1.98	
26.	6.7	" $\frac{M}{10}$	>11	.482	18.5	17.60	35.0	38.1	

Continued p113.

TABLE I. Water and Univalent Cations. (Cont.)

No.	Date	Nature of Solution.	pH Soln.	Dry Wt.	°C 8R	T_{250}	F	Fall %
27.	1.6	NaOH $+Na_2SO_4$ $\frac{M}{50}$	>9.3	.496	17.8	16.50	31.3	37.3
28.	1.6	" $\frac{M}{200}$	>9.3	.491	17.7	17.36	33.2	35.5
29.	1.6	" $\frac{M}{1000}$	9.3	.490	17.7	21.20	32.8	36.2
30.	1.6	" $\frac{M}{5000}$	7.1	.490	17.8	25.05	48.2	6.5
31.	3.7	H_2SO_4 $\frac{M}{20,000}$	5.0	.498	16.0	29.30	53.0	6.44
32.	5.7	" $\frac{M}{100,000}$	6.3	.486	16.2	30.45	56.7	0.14
33.	3.7	HCl $\frac{M}{10,000}$	5.0	.492	16.0	30.89	56.5	0.18
34.	6.7	$H\bar{A}c$ $\frac{M}{10}$	3.0	.485	18.45	15.80	31.2	44.9
35.	6.7	Na_4FeCy_6 $\frac{M}{10}$	>8.4	.487	18.4	17.90	35.2	37.9
36.	28.5	Na_2SO_4 $\frac{M}{50}$ Gel	6.6	.506	18.4	15.40	29.1	43.5
37.	28.5	" $\frac{M}{200}$ "	6.6	.495	18.4	16.35	31.6	38.6
38.	28.5	" $\frac{M}{1000}$ "	6.6	.490	18.7	20.15	39.6	23.0
39.	28.5	" $\frac{M}{5000}$ "	6.6	.487	18.7	24.70	48.9	5.04

TABLE II. Bivalent Cations.

No.	Date	Nature of Solution.	pH Soln.	Dry Wt.	°C 8R	T_{250}	F	Fall %	
1.	19.6	$CaCl_2$ M/50	6.7	.503	21.2	14.94	30.4	46.2	
2.	19.6	" M/100	6.4	.504	21.1	14.60	29.6	47.7	
3.	21.6	" M/200	6.4	.507	18.9	16.1	30.8	45.6	
4.	21.6	" M/400	6.3	.509	19.1	16.5	31.6	44.2	
5.	21.6	" "	6.7	.492	19.1	17.15	33.9	40.1	
6.	22.6	" M/1000	6.7	.494	19.8	18.1	36.3	35.9	
7.	22.6	" M/2500	6.3	.493	20.0	20.0	40.3	28.7	
8.	22.6	" M/5000	6.3	.492	19.9	22.1	44.6	21.2	
9.	23.6	" "	6.8	.505	18.6	23.0	43.7	22.8	
10.	22.6	" M/10,000	6.3	.487	19.9	22.9	46.8	17.4	
11.	23.6	" M/20,000	6.6	.504	18.7	25.4	48.6	14.2	
12.	26.6	" M/50,000	6.6	.496	19.2	25.8	50.7	10.3	
13.	2.7	" M/100,000	6.1	.483	17.2	30.3	58.3	2.94	Rise.
14.	25.6	$Ca(OH)_2$ M/500	>9.3	.524	18.2	17.5	31.7	44.0	
15.	26.6	" M/2500	9.1	.491	19.2	21.2	42.1	25.5	
16.	25.6	" M/5000	7.2	.486	18.3	21.8	42.8	24.3	
17.	24.6	$BaCl_2$ M/5000	6.2	.485	20.0	21.5	44.1	22.1	
18.	24.6	" "	6.6	.483	19.9	21.2	43.6	22.9	
19.	25.6	$MgSO_4$ M/500	6.8	.488	18.2	17.5	34.2	39.6	
20.	25.6	" M/5000	6.6	.538	18.4	24.7	43.9	22.5	
21.	24.6	$Co(NO_3)_2$ M/5000	7.0	.482	20.0	21.5	44.3	21.7	
22.	24.6	" "	6.4	.472	20.1	21.9	46.3	18.2	
23.	26.6	$CuSO_4$ M/5000	6.6	.491	19.0	20.5	40.5	28.4	

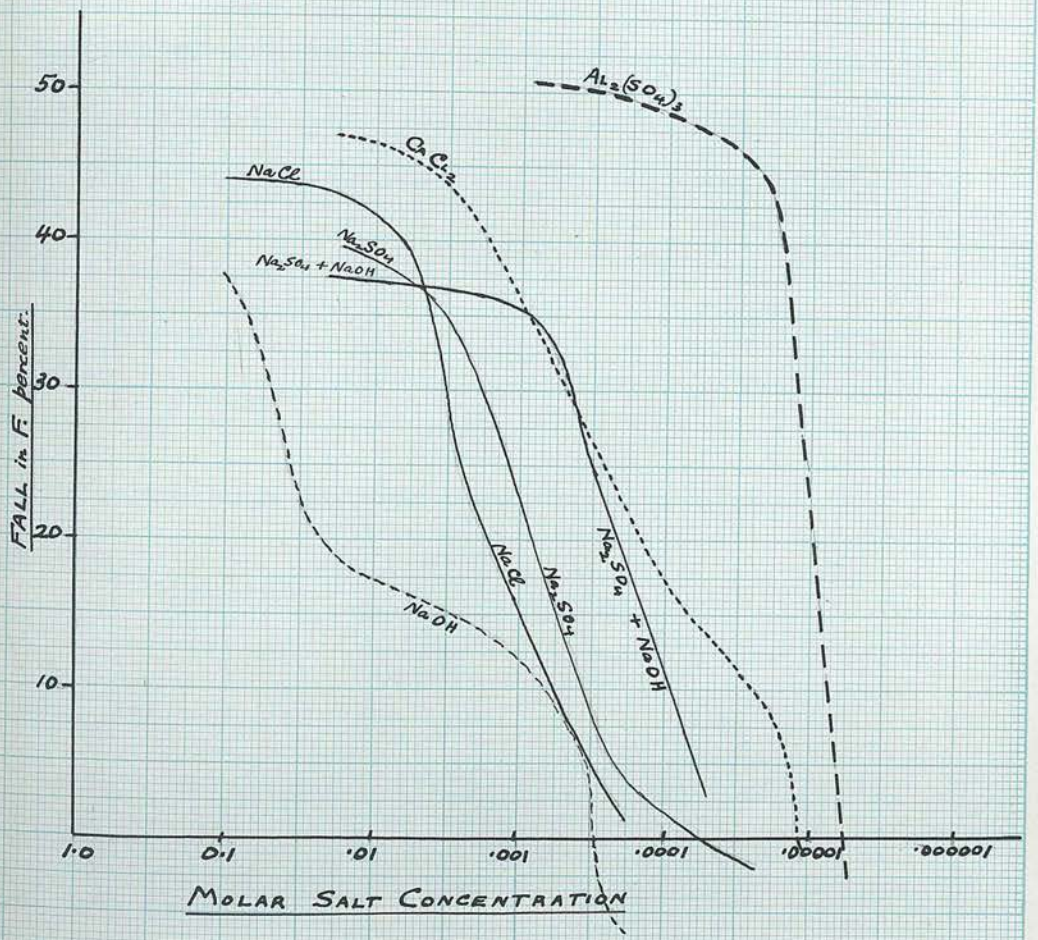
TABLE III. Tervalent Cations.

No.	Date	Nature of Solution	pH Soln.	Dry Wt.	°C 8R	T_{250}	F	Fall %	
1.	28.6	$Al_2(SO_4)_3$ $\frac{M}{1000}$	4.3	.494	17.5	14.81	28.0	50.4	
2.	28.6	" $\frac{M}{5000}$	4.65	.491	17.4	15.55	29.6	47.8	
3.	28.6	" $\frac{M}{20,000}$	5.0	.494	17.4	14.80	28.0	50.5	
4.	29.6	" "	5.1	.511	20.8	13.8	27.4	51.6	
5.	29.6	" "	5.1	.497	20.8	13.9	28.4	49.9	
6.	29.6	" $\frac{M}{50,000}$	5.5	.489	20.8	14.65	30.4	46.3	
7.	29.6	" "	5.5	.500	20.8	14.62	29.7	47.6	
8.	28.6	" $\frac{M}{100,000}$	6.2	.493	17.5	27.9	52.9	6.58	
9.	30.6	" "	6.0	.500	18.1	22.65	43.0	24.0	
10.	30.6	" $\frac{M}{200,000}$	6.4	.508	18.3	31.15	58.5	3.36	Rise
11.	30.6	" "	6.4	.492	18.1	28.77	55.6	1.86	
12.	30.6	" $\frac{M}{500,000}$	6.3	.498	18.3	30.57	58.6	3.48	Rise
13.	3.7	Chrome Alum $\frac{M}{10,000}$	4.8	.495	15.8	20.67	37.4	33.9	
14.	1.7	" $\frac{M}{50,000}$	5.7	.500	19.8	23.85	47.2	16.5	
15.	1.7	" "	5.7	.501	19.7	22.4	44.2	22.0	
16.	2.7	" $\frac{M}{100,000}$	6.2	.489	17.2	28.06	53.7	5.12	
17.	3.7	$FeCl_3$ $\frac{M}{10,000}$	5.0	.497	15.9	15.65	28.3	50.1	
18.	1.7	" $\frac{M}{50,000}$	6.1	.504	19.7	21.1	41.3	27.0	
19.	1.7	" "	6.1	.499	19.8	23.0	45.6	19.4	
20.	2.7	" $\frac{M}{100,000}$	6.1	.491	17.3	31.17	59.0	4.24	Rise

IONIC COAGULATION EFFECTS

on

Beaten Cellulose Suspensions.



The foregoing diagram gives the main results of the preceding tables graphically. Ordinates represent fall in flow constant due to the amount of salt denoted on the logarithmic scale of the abscissae. The logarithmic scale is merely used for convenience. The figures in the tables do not fit the curves very well, but certain broad inferences can be drawn.

Conclusions regarding the Valency Effect of the Cation.

(1) Minimum concentrations necessary for a coagulation effect on the pulp cake within say about 10% of the maximum are grouped according to the valency of the cation.

(univalent $\frac{M}{500} - \frac{M}{2000}$

(bivalent $\frac{M}{500} - \frac{M}{2000}$

(tervalent $\frac{M}{50,000}$

(2) Concentrations (maximum) which will produce no effect are

(univalent $\frac{M}{3000} - \frac{M}{10,000}$

(bivalent $\frac{M}{50,000} - \frac{M}{100,000}$

(tervalent $\frac{M}{200,000}$

(3) The OH' ion in NaOH stabilises to some extent, but not in $Ca(OH)_2$. The stabilising effect is lost when Na_2SO_4 is present.

(4) No significance can be attached to apparent peptisation effects.

(5) Within the concentration range where change in coagulation effect is rapid, it is difficult to obtain concordant results.

(6) The magnitude of the maximum coagulation effect seems to vary slightly with the valency of the cation and is appreciably greater for $Al_2(SO_4)_3$ than for NaCl. (c.f. viscosity experiment p.106 this part using concentrated NaCl solution.)

(7) It is not possible with this apparatus to correlate pH value and coagulative action.

(8) There is need to go again into the question of whether protection and peptisation phenomena occur with beaten pulp suspensions.

4. Peptisation and Protection Effects.

As can been seen from the tables on page 111 a spontaneous change in the direction of increasing flow constant , which is a change analogous to a peptisation process, occurs very slowly with well beaten pulps. The change slows up as time advances and probably has definite limits. The term peptisation is admittedly applied here in a loose manner as meaning the reverse of what has been called coagulation. The tables suggest that a similar process takes place much more rapidly in the presence of salts in concentrations insufficient to cause coagulation. The effect is most irregular however, and a further series of experiments was undertaken, September - October 1926, to see if it would be more definitely established. The results were again extremely irregular, and similar to those found in the preceding tables. The pulp used was beaten for 15 hours in a pebble mill and showed a Schopper Riegler wetness figure of 91.5° and a flow constant of 44. This latter

figure increased to 57 in the course of 3 weeks. The peptisation effect when observed was comparatively slight.

It was next considered desirable to see if the addition of small quantities of gelatine sol could inhibit the coagulative action of salts. The first experiments were done with gelatine which was not free from electrolytes. (See Table on univalent cations, end of table.) A reliable pure sample of gelatine was obtained later and the following series of experiments were done on pulp Cc milled 16 hours and showing Schopper Riegler wetness of 88°. The pH values were all between 6.2 and 6.6 and the dry weights of pulp used about 0.8 gms. All the experiments were done in duplicate, deviations from the mean being as shown in the table.

Date 1927	Protective Colloid	Coagulant	F	Devn. of F	Fall %	
24.1	Nil	Nil	28.18	1.10	-	
25.1	"	"	29.52	1.70	-	
25.1	"	$Al_2(SO_4)_3$ $\frac{M}{10,000}$	13.05	.08	55.0	
27.1	.0005 gms.1 dy.	" "	12.17	1.00	58.0	
27.1	.0025 gms.1 dy.	" "	11.28	.08	61.1	
1.2	.02 gms.2 dys.	" "	10.92	.37	62.3	
26.1	Nil	" $\frac{M}{50,000}$	27.20	1.31	6.2	
1.2	"	Na_2SO_4 $\frac{M}{1000}$	25.92	.53	10.6	
3.2	"	" $\frac{M}{2000}$	24.41	.06	15.8	
1.2	.0025 gms.2 dys.	" $\frac{M}{1000}$	26.02	.27	10.3	
31.1	.02 gms. 12 hrs.	" $\frac{M}{2000}$	29.73	1.59	2.5	Rise

cont. p119.

Date 1927	Protective Colloid.	Coagulant	F	Devn. of F.	Fall %	
3.2	.02 gms. 12 hrs.	Na_2SO_4 $\frac{M}{2000}$	34.31	3.0	18.3	Rise
26.1	.0025 gms. 12 hrs.	Nil	34.07	.49	17.5	Rise

The protective colloid was gelatine and the above table records the weights used for each test, and the period of steeping of the pulp. The gelatine was always added first, and then the coagulant. It must be concluded that the protective effect is just probable in the last two cases but cannot be held to be established. The viscosity of the solutions was found to be unaltered.

5. Effect of Boiling Pulp Suspensions in Water.

If the stuff will not part quickly with its water of suspension on the wire of the paper machine, production may be slowed up. It is often the practice in such cases to blow steam into the stuff to warm it up. The drainage of the pulp on the wire is thus greatly improved. This result is to be expected owing to the diminished viscosity of water at higher temperatures, but several authorities claim that a dehydrating action also takes place. It was therefore decided to try the effect on the flow-constant, of boiling in water for a short period and cooling to normal temperature before testing. It was at once obvious that such a treatment caused a considerable fall in the flow-constant. The phenomenon seemed to be exactly similar to the coagulation produced by electrolytes. A considerable fall was already obvious after steeping for 30 minutes in water at 70°C, and the

difference between the effects of boiling for 30 minutes or so and boiling under a reflux for 8 hours was not great. The greatest effect of all was obtained by boiling in the presence of $\frac{M}{1300}$ $Al_2(SO_4)_3$ solution. It was next discovered that the pulp which had been boiled in pure water tended in the course of steeping at ordinary temperatures to revert to its original condition before treatment. The period of recovery might be as much as 30 days. In the case of pulp which had been coagulated by electrolytes no such reversion took place. The effect of freezing and alternate thawing out of the pulp was tried in the winter of 1925 - 26, but as no special refrigerating apparatus was available natural cold was used. The temperature fell to $-3^{o}C.$ - $-8^{o}C.$ during the nights when the experiments were done. After 3 or 4 treatments the flow-constant was redetermined and was found to remain unaffected. It must be admitted that even a temperature of $-10^{o}C.$ may be insufficient to freeze the water in the finest pulp capillaries. The appearance of the pulp when frozen was hard enough however. The matter was not deemed of sufficient interest or importance to be pursued further. It was considered that an increase of flow constant might be expected to result from the freezing process. The results of the freezing experiments have not been recorded in the following tables.

The tabulation is essentially similar to that used for the ionic coagulation effects. In all cases the dry weight of pulp used was between 0.96 and 1.00 gm.

The pulp used was kollerganged for 5½ hours. No Schopper-Riegler test is available.

No.	Date.	Conditions of Treatment of Pulp	Flow Temp. °C	Uncorrected Flow Time. Av.	Devn.	F	Fall in F %
1.	20.10	Pure Water	18.2	18.38	.72	17.70	
2.	22.10	" "	18.8	16.17	.34	15.78	
3.	26.10	Steep 1 hr. 50°C.	17.8	18.02	1.09	17.23	
4.	30.11	No 3 treated, stored 35 dys.	18.2	17.03	.48	16.59	
5.	22.10	30 mins. 70°C	19.6	11.77	.17	12.07	27.9
6.	21.10	30 mins. 90°C	19.2	11.95	.33	11.97	28.5
7.	23.10	30 mins. at 90°C. Boil 20 mins.	19.6	8.88	.02	8.91	46.8
8.	28.10	Boil 30 mins. Store 8 dys.	16.0	12.63	.33	11.45	31.6
9.	27.10	Boil 8½ hrs.	18.1	9.05	.07	8.71	48.0
10.	1.12	No.9 stored 35 dys.	18.1	17.93	1.50	17.36	3.7 Rise
11.	24.10	Steep $\frac{M}{1300}$ $Al_2(SO_4)_3$	20.1	7.37	.56	7.39	55.9
12.	28.10	Boil 6 hrs. in $\frac{M}{1300}Al_2(SO_4)_3$	17.7	6.00	.20	5.64	66.3
13.	1.12	No. 12 stored 34 dys.	18.3	6.40	.42	6.22	62.8

Notes on the above Table.

(a) The pulp is tested at once after the stated treatment has been completed. In every case the pulp has been cooled before testing. The boiling is conducted in a volume of water suitable for the subsequent flow test, i.e. 700 cc. for a pair of tests.

(b) All tests have been done in duplicate, the deviation from the mean of the uncorrected flow time being recorded

in the appropriate column.

(c) The Fall in F is calculated on an average F_{aq} value of 16.74. The deviation from the mean attached to this number is 0.96 or 5.7%. Thus it is never possible to state absolutely that the boiling and steeping process can have an ultimate peptising effect. Of course the value of F_{aq} itself increases slowly with time.

(d) This series of experiments was satisfactory as regards regular conditions of flow.

(e) It cannot be definitely stated that the coagulation change due to heating in water takes place suddenly between 50°C and 70°C. The change may be a slow one at 50°C. and may gradually accelerate up to 100°C. Different pulps may behave in a different manner.

(f) The combined effect of boiling in water and adding a suitable electrolyte is greater than either effect by itself.

(g) The addition of a coagulating electrolyte definitely prevents reversion to the original condition on the part of the pulp.

6. The Lyotrope Series Effect.

As it seemed probable that the slow increase of the flow-constant on prolonged steeping of beaten pulp in water was due to the development of a swollen colloidal surface film on the finer fibres, it was thought desirable to find out if this effect could be accelerated or inhibited by fairly strong salt solutions, according to their position in the Hofmeister or lyotrope series. Very good results were hardly to be expected, as the peptising effect if any would be opposed by the strong

coagulating action of the cation in the salt solution. For the same reason it was considered unlikely that the less well-marked differences of the cations in the lyotrope series of univalent ions would give any result at all. In any case only $Na^{\cdot}$, $K^{\cdot}$, and $(NH_4)^{\cdot}$ were available and the last was known to be somewhat unsatisfactory, as strong solutions of ammonium salts in presence of air showed a tendency to dissolve traces of copper from the metal of the testers and wires. Also it will be seen from the table on the coagulating action of the bivalent ions that there is little difference between the effects of $Ca^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, and $Mg^{\cdot\cdot}$.

It was therefore resolved to work with fairly strong solutions of univalent alkali metal salts with different anions. The first series of experiments was done on a pulp with F_{aq} = 150, and the effect of steeping the pulp for 10 - 11 days in M/2 solutions of NaCNS, KI, Na_2SO_4 and Rochelle salt was examined by subsequently determining the flow-constants in M/5 solutions of the same salts. The actual flow-constants varied from 84.3 to 85.9 and were deemed to be essentially identical.

A series of experiments was therefore undertaken at somewhat higher salt concentrations. In some cases the effect of steeping for 8 hours at $70^{\circ}C$ was studied. In all cases experiments were done both on the acid and alkaline sides of neutrality, and the pH values were recorded. Under each set of conditions a pair of exact duplicate experiments were done, the deviations from the mean being recorded. As the stronger salt solutions

showed appreciable divergences in viscosity from pure water, each experiment was accompanied by a determination of the relative viscosity/density ratio to that for water at 20.2°C. This was subsequently used in calculating the corrected final values of F in each case. The salts used were NaCl, Na_2SO_4, $Na(CH_3COO)$ and NaCNS. For the room temperature experiments the pulp was steeped for 48 hours in the salt solution. The results are given in the following table.

No.	Date 1926	Salt Solution, Conditions	Viscometer Secs.	°C	Rel. $\frac{\eta}{\Delta}$	pH
1.	23.3	NaCl M alkaline	64.7	17.5	1.040	8.2
2.	27.3	" " "	68.0	15.3		9.3
3.	23.3	" " acid	65.5	17.3	1.044	6.8
4.	27.3	" " "	68.2	15.2		5.0
5.	24.3	Na_2SO_4 .8M Alk. hot	80.8	14.7	1.272 as acid	9.3+
6.	26.3	" .67M " cold	not done			9.3+
7.	24.3	" .8M acid hot	80.9	16.5	as alk.	4.0
8.	26.3	" .67M " cold	78.1	16.2	1.214	4.4
9.	24.3	NaAc. M alk.	72.4	17.6	1.172	9.3 +
10.	24.3	" " acid	71.8	18.0		5.4
11.	25.3	NaCNS M alk.	61.6	15.8	.948	8.0
12.	25.3	" " acid	59.6	16.9		4.5

This table is concluded on the next page with the corresponding reference numbers on the left hand column.

Notes.

(a) Hot and Cold refer to a steeping period at 70°C for

8 hours and one at normal temperature for 2 days respectively.

(b) The alkaline and acid conditions are obtained by adding sufficient of the corresponding alkali or acid to produce the desired change in pH value. For $Na(C_2H_3O_2)$ this means caustic soda or acetic acid.

(c) The NaCNS solutions attacked the copper and possibly the other metals of the tester to some extent.

(d) The fall in F in the last column of the second table is based on a value of 153.3 for F_{aq}.

Continuation of table on previous page.

No.	Dry Wt.	°C Flow.	Flow Time uncorrected	Devn.	F	Fall in F, %	Solution.
1.	.266	17.3	23.36	.56	78.36	48.9	M NaCl alk
2.	.332	16.2	23.61	.19	71.42	53.4	" " "
3.	.278	16.8	26.32	.07	82.89	45.9	" " acid
4.	.291	16.2	29.01	.62	81.88	46.6	" " "
5.	.270	16.4	20.07	.13	53.16	65.3	.8M Na_2SO_4 alk Hot
6.	.300	17.5	26.37	one only	58.39	61.9	.67M " " Cold
7.	.270	16.3	23.10	.60	61.04	60.2	.8M " ac. Hot
8.	.278	17.4	26.58	.02	77.60	49.4	.67M " " Cold
9.	.278	17.1	26.35	.45	75.10	51.0	M NaAc. alk.
10.	.266	16.9	28.12	.23	83.23	45.7	" " acid
11.	.287	17.3	27.31	.42	92.91	39.4	M NaCNS alk.
12.	.285	17.0	27.53	.04	94.32	38.5	" " acid

The problem is a fairly complicated one, but the above figures suggest that in strong solutions Na_2SO_4 has a more powerful and NaCNS a less powerful coagulating effect than NaCl or NaAc. solutions. This is in accordance with what would be expected, assuming that a lyotrope series effect exists in this case. In more dilute solutions there does not seem to be any effect owing to the powerful coagulating effect of the cation. No more can be expected of results obtained by the flow-constant method. The lyotrope series effect will be gone into again in the second experimental part of this paper, and by quite another method.

7. Hydration with concentrated Salt Solutions.

A few experiments were done by the flowmeter method on pulps which had been treated by boiling concentrated $Ca(CNS)_2$ solution and by the viscose and cuprammonium solvent reagents respectively. The solvent treatment was only partial, but sufficient to cause considerable swelling. Before determining the flow constant the pulp was very considerably diluted with distilled water, and thoroughly washed on a wire sieve. It was then shaken up and thoroughly defibrated with glass beads. In every case the flow constant was enormously reduced. The original F_{aq} was 44.5. The thiocyanate experiments gave values of F ranging from 20 down to 6, and in the latter case the pulp was badly and irreversibly agglomerated. The cuprammonium and viscose results were similar. On the other hand, if the pulp was tested in the flowmeter in presence of the solvent after only slight dilution, the value of F was often very high and the pulp

practically undrainable. Nakano's recent experiments (138) show that it is very difficult to get the wet beating effect on a pulp which has been partially swollen by one of the above solvents, reverted and thoroughly washed.

8. Adsorption of Salts from Solution by Beaten Pulp.

In the course of the experiments on the coagulating effects of the different ions some measurements were made on the adsorption of the ions by the pulp cake. The only anion to be dealt with was the Cl' in the case of NaCl solutions. No adsorption of Cl' was observed. Several experiments were done on the adsorption of NaOH by a titrimetric method. It was clear that the $(OH)'$ was being removed in this case by some potentially active acidic residue in the sulphite pulp. In the case of the experiments with $CuSO_4$ there was distinct evidence of adsorption, but even at $\frac{M}{5000}$ $CuSO_4$ strength the removal of the Cu'' by the pulp was incomplete. In the case of $FeCl_3$ however the removal was practically complete when the solution strength was $\frac{M}{10,000}$. The adsorption is always more complete with well beaten than unbeaten stuff, and the difference is considerable. Before adopting the flow-meter method the author did quite a number of experiments on the relative adsorptions of ferric salts and typical dyes by beaten and unbeaten pulps respectively. This line of research seemed unpromising and was not followed up. It was found however that basic dyes such as malachite green showed little difference towards beaten and unbeaten pulps, acid dyes such as picric acid were slightly more adsorbed by the

well-beaten pulp, and certain substantive dyes such as Congo Red were considerably more adsorbed by the beaten pulp. The purity of the Congo Red and the Malachite Green was not above reproach however. One typical experiment with ferric sulphate solution will be cited.

Unbeaten Pulp	Original solution	0.035% Fe
	Filtrate	0.027% "
	On the dry pulp adsorbed	0.336% "
Beaten Pulp	Filtrate	0.0175% Fe
	On the dry pulp adsorbed	0.677 % "

The process is probably one of hydrolysis as well, and it is not clear whether it is $Fe^{\cdot\cdot\cdot}$ or $Fe(OH)_3$ or some basic salt which is taken up. The filtrate from the beaten pulp shows a greater tendency than the original solution (diluted to the same degree) to throw down a precipitate of $Fe(OH)_3$ spontaneously.

Experiments also showed the remarkable power, of beaten pulp especially, of bringing the pH value of water which had been filtered through the pulp cake nearer to neutrality. Of course the water must be practically unbuffered to show this effect. Thus there exists in the fibrous cellulose used in this investigation a strong adsorptive capacity for $H^{\cdot}$ or $(OH)^{\cdot}$ ions. This is still evident when the ash content of the fibre has fallen to 0.15%. No work has been done on the question of whether this is a base-exchange phenomenon or not.

9. Flow Tests in Alcohol and Alcohol-Water Mixtures.

The flow constant method has been shown to be applicable to testing other than aqueous suspensions. It has already been shown that experiments in ethyl alcohol and glycerol solutions give abnormally low flow-

constants after correction for the viscosity/density ratio of the liquid. The divergence from the flow-constant for water is so considerable that it is extremely unlikely that the results can be explained by the breakdown of Poiseuille's law, as the latter holds fairly accurately over the range of water viscosities between temperatures of 10°C and 25°C. Glycerol solutions have not been thoroughly studied. The case of ethyl alcohol has been closely investigated both from the point of view of the reversibility of the changes and of their magnitude for a graded series of mixtures of alcohol and water.

In the case of ethyl alcohol the ratio of the corrected values of F_{aq} to F_{alc} is often somewhere about 15. It is only reasonable to suppose that the alcohol has exerted a dehydrating action on the fibre. A great many determinations have been made of the values of F_{aq} and F_{alc} for different beaten pulps. If the dehydrating action of alcohol is complete, the value of F_{alc} will be a measure of the degree of dispersion of the pulp unaffected by hydration, and the comparative difference of F_{alc} and F_{aq} will be a measure of hydration. This matter will be discussed again in the second experimental part of this paper.

Industrial Alcohol was used for this part of the work. This liquid was quite neutral in reaction, and contained about 5% of water and a slightly lesser quantity of methyl alcohol and other denaturants. For certain experiments this was redistilled twice over quicklime

with the production of a 96% alcohol.

The question of the reversibility of the dehydrating action of alcohol was examined with several pulps. Several variations were found, and there was some evidence that a water beaten pulp after being dehydrated in industrial spirit did not completely recover its flow-constant when immersed in water. In most cases the differences were not large, and it must always be remembered that the process of dehydration in alcohol will remove a certain proportion of residual resinous constitutents from a sulphite pulp. In many cases the differences between the flow constants, where the equilibrium had been approached from opposite directions, was well within the limits of experimental error. Where the pulp had a very high value of F_{aq} the differences were larger. In one case where F_{aq} was 150 the values of F in a 40% solution of alcohol by weight were 87.8 and 76.5 respectively. The lower value was reached if the pulp passed through an intermediate dehydration stage. In another test a pulp Cb was used which was pebble-milled with industrial alcohol instead of water for 30 hours. The wetness test in water was 88.4° (S.R.) (= Schopper Riegler.)* F_{aq} = 32.2 F_{alc} = 2.76. The value of F for 50% alcohol was approached from both directions and the two figures showed a deviation from the mean of only 8%. (F = 4.96). That pulp which had previously been steeped in water gave the higher value of F. Generally speaking therefore the dehydrating

* In future S.R. = Schopper-Riegler degrees.

action of alcohol on the flow-constants of pulps is quite reversible.

It is therefore in order to investigate the variation in flow-constant in graded alcohol-water mixtures, irrespective of the side from which the equilibrium is approached. The following two tables give the results of two such series of experiments. The pulps used were (a) a long fibred pulp well beaten in the pebble mill to 87° wetness S.R. and another (b) more drastically beaten to 91°. The tabulated results will be graphed along with certain corresponding results on the effect of alcohol-water mixtures on the cohesion properties of pulps. (See IX p. 158A)

Dehydration of pulp (a) in alcohol-water mixtures.

Alcohol %	Viscometer Secs.	°C.	T_{250}	°C	Dry Wt.	F	% F Devn.	Relative F
0			24.60	18.6	.997	23.72		
0			20.86	18.4	1.019	19.59	9.2	100
0			20.35	18.8	.789	24.92		
10	94	17.0	14.55	17.1	.569	16.35		71.9
20	122	19.9	16.59	20.0	.814	9.85		
20	"	"	17.91	20.0	.820	10.81	4.6	45.4
30	161	18.6	12.01	19.6	.843	5.32		
30	159	19.2	13.20	19.6	.818	6.03	6.2	24.9
40	180	18.0	10.19	17.9	.808	4.11		
40	182	17.9	10.07	18.0	.799	4.07	0.4	18.0
50	193	16.3	17.52	17.4	1.260	4.34		
50	191	16.5	16.29	17.4	1.226	4.17	2.0	18.7

Cont. p 132.

Alcohol %	Viscometer Secs.	°C	T_{250}	°C	Dry Wt.	F	% F Devn.	Relative F
71	156	17.7	10.47	17.4	1.646	2.37)		
							)6.0	9.83
71	165	16.2	9.60	17.4	1.677	2.10)		
90	109	19.2	5.41	19.3	1.890	1.54)		
							)11.0	6.09
90	108	19.6	4.45	19.2	1.951	1.23)		

Notes.

(i) For 0, 10, 20% alcohol the ratios of 8th. to 7th. flow time are rather high. This is again so at 40%. Flow measurements are often difficult in alcohol-water mixtures owing to the slow settling of the fibres.

(ii) The last column gives the average values of F in each case relative to a value of F_{aq} = 100.

Dehydration of Pulp (b) in alcohol-water mixtures.

Alcohol %	Viscometer Secs.	°C	T_{250}	°C	Dry Wt.	F	% F Devn.	Relative F
0			17.54	19.3	.216	79.44)		
0			18.5	18.5	.248	71.53)	4.9	100
0			20.5	18.5	.244	80.63)		
10	93.3	17.0	24.2	16.9	.189	80.36		104
20	124	19.7	32.6	19.8	.212	72.34)		
							)7.0	100.7
20			33.76	19.8	.209	83.20)		
30	176.4	16.5	36.4	15.3	.205	57.69)		
							)3.5	72.2
30			36.2	15.3	.219	53.73)		
40	190	17.0	20.17	18.1	.200	31.78)		
							)3.6	39.7
40			18.41	18.0	.198	29.57)		

Cont. p133.

Alcohol %	Viscometer Secs.	°C	T_{250}	°C	Dry Wt.	F	% F Devn.	Relative F
50	193.5	16.5	30.4	17.2	.350	26.71	1.5	34.1
50			29.4	17.1	.351	25.90		
70	166.6	16.0	7.20	14.7	.383	6.446	0.4	8.32
70			7.10	14.8	.380	6.397		
90	112.7	18.5	4.31	17.9	.390	5.662		
90			4.40	17.8	.412	5.475	6.5	6.77
90	111.6	19.7	7.05	19.5	.808	4.573		
90			8.23	19.4	.826	5.196		
96	99	17.0	8.49	16.3	.737	6.67	2.5	8.43
96			8.67	16.4	.792	6.35		

Notes. (Cont. from p. 132)

(iii) The deviation column represents the mean deviation from the average value of F expressed as a percentage of that value.

(iv) The alcohol solution strengths are not known with great accuracy as the composition of the industrial spirit is not exactly known. The percentages in the first column are percentages by weight on the total weight of solution. The density was used only as a check.

(v) In the second table the anomalous results with the 96% alcohol were obtained a month later than the others (April 1928). A comparative pair of tests with 90% alcohol was however done immediately afterwards and the average value F = 5.22 obtained, this being the same

as for the 4 tests given in the table.

It is clear therefore that the drainage behaviour of well beaten pulps in 100% alcohol requires some further investigation. If this were done however it would have to be with a purer grade of alcohol than industrial spirit. It is possible that the anomaly might then vanish. At the date of this last experiment interest was centred on another side of the problem, and the matter was not pursued further.

(vi) The great differences in dehydration behaviour of the two pulps are not readily explicable. The dehydrating action of alcohol is not always immediately complete or immediately reversible. In one other case a pulp gave a decrease in F of nearly 15% when dehydrated and then immersed in water so that the alcohol concentration was only 2%. The practice in all the above experiments has been to wash the pulp on a Buchner funnel with gradually increasing percentages of alcohol, and so to arrive at the desired composition. The pulp was then dispersed in this liquid by shaking with glass beads. It must be admitted that the method of dispersion itself can affect the final flow-constant, but no other method seemed to be available when working with such a liquid as alcohol.

(vii) It is not alleged that the presence of a very small percentage of alcohol can exert a hydrating action, although this is stated to be the case both for alcohol and glycol in the case of certain lyophilic colloids.

10. Ionic Coagulation in Alcohol and Alcohol-Water Mixtures.

It was considered desirable to find out if ionic coagulation takes place in 90% alcohol suspensions. The first set of experiments done in December 1926 was not altogether satisfactory, but indicated that there was an ionic coagulation effect. The choice of electrolyte is evidently restricted in 90% alcohol and very strong solutions were used for the first experiments. The pulp used had the value F_{alc} = 2.76 and this was reduced to 2.31 after boiling for 2 hours in industrial alcohol under a reflux and cooling. The addition of HCl and NaOH to two portions of pulp in a concentration of M/120 lowered the value of F to 2.10 and 2.00 in two pairs of experiments. No neutral salt experiments were done.

It was considered that the experiments should be repeated and extended in order to see if Kruyt's theory of the stability of lyophilic colloids could be extended by analogy to the case of beaten cellulose suspensions. A rather better pulp was used from which most of the resinous constitutents had been extracted prior to bleaching and beating. The pulp was gently treated in the pebble mill for about 50 hours to preserve length of fibre, and gave a wetness reading of 93° (S.R.) and a value of F_{aq} = 129.5. These experiments were done in February 1932 using a 95% rectified spirit. The coagulating effect at 95% alcohol was studied in M/200 $NaClO_3$ solution. Another set of experiments was done in a 40% by weight solution of alcohol in water using

M/500 and M/1000 solutions of NaCl. The corresponding experiments with the NaCl were then done in aqueous solution. Lastly one or two experiments were done with tannic acid in aqueous solution, as Kruyt found that this substance was strongly adsorbed at the surface of such lyophilic colloids as agar with a resulting dehydrating action. The results of all the experiments are given in the following table.

Ionic Coagulation in Water and Alcohol.

Liquid	Viscometer Secs	Viscometer °C	Dry Wt.	°C	T_{250}	F	F Devn. %	F Fall %
Water			.180	16.4	26.4	129.5	3.0	0.0
M/1000 NaCl aq.			.180	16.7	18.3	92.7	1.2	28.4
M/500 "			.180	19.3	16.0	86.3	.94	33.4
.012% Tan. aq.			.180	17.2	25.2	129.5		0.0
.25% "			.180	18.6	13.4	71.3		45.0
Alcohol R.S.	117	18.1	.566	18.1	21.05	18.44	2.5	0.0
M/200 $NaClO_3$ "	120	16.9	.529	18.8	18.8	17.86	4.5	3.1
40% alc.	184.5	16.7	.1125	16.5	30.2	84.1	0.1	0.0
+ M/1000 NaCl	178.9	18.1	"	18.1	19.9	57.3	2.3	31.8
+ M/500 NaCl	186.4	16.4	"	16.3	21.3	58.6	0.0	30.3

- Notes on Table -

(a) The first 5 lines describe experiments in aqueous solutions, all being duplicate experiments except those with tannic acid marked Tan. aq.

(b) The next two lines denote experiments in neutral rectified spirit (R.S.), in which $NaClO_3$ is soluble.

(c) The last three lines describe experiments done in 40% alcohol solution.

(d) In the last column the fall in F percentage is reckoned on the value of F for water, R.S. and 40% alcohol respectively.

It is evident that there is hardly any ionic coagulation effect for fibre suspensions in 95% alcohol and that for 40% alcohol the effect is the same as for aqueous solutions. Tannic acid does not appear to have a dehydrating action on fibres. Of course it is quite obvious that it is a very different thing to measure the drainage properties of cellulose fibres and the precipitation properties of such a substance as agar or gelatine.

11. Flow Tests on Asbestos Suspensions.

Before concluding the work on beaten cellulose by the drainage method, a number of experiments were done on good quality Gooch asbestos. This was so long fibred that it was necessary to give it a thorough treatment in the pebble mill before it would form a good cake. The treatment will be described in the second experimental part of this paper, as the beaten asbestos was also used for volume contraction or cohesion tests. The asbestos suspensions showed a somewhat anomalous behaviour. All the experiments were reasonably satisfactory, although the values of F were so low that the most satisfactory flow conditions could not be obtained.

First Series.	
No.	F
1. Distilled Water	2.60
2. Boiled & cooled (water)	3.06
3. Steep $\frac{M}{1000}$ $Al_2(SO_4)_3$ Soln.	6.36
4. Industrial Alcohol	2.91
5. NaOH Soln. $\frac{M}{200}$	3.39
Second Series.	
No.	
1. Distilled Water	4.00
2. Industrial Alcohol	3.86
3. $\frac{M}{1000}$ $Al_2(SO_4)_3$ Soln.	14.94
4. $\frac{M}{200}$ NaOH Soln.	4.20
5. Dried at 110°C and repulped	7.54

The results are quoted in order to show the contrast with beaten cellulose. There is obviously no dehydration effect with alcohol and no ionic coagulation effect.

The anomalous effect with aluminium salts cannot be explained here. All the experiments have been done in duplicate with fair agreement, and the two series correspond to two different batches of asbestos after treatment in the pebble mill. The asbestos pulps gave readings of 65° and 75° respectively on the Schopper-Riegler wetness tester.

12. The Schopper Riegler Tester.

It may be as well to point out the results obtained with the Schopper Riegler beating degree tester in the case of some of the phenomena which have been studied

with the flow-meter.

It is obvious of course that this tester cannot give accurately comparable results with different weights of pulp and with liquids of different viscosity. But some sort of difference will be recorded. For instance, a certain pulp tested 88.4° in water and 63.5° when run through the instrument in suspension in industrial alcohol. The dehydration effect is therefore much less striking and it is not possible to make use of the result. In like manner it is very troublesome to correct S.R. figures for widely different weights of pulp used in any tests.

A number of experiments were done on the ionic coagulation effect using the S.R. tester. It was necessary with wet beaten pulps to use such weights of pulp as would give a volume of nearly 500 cc. of fast draining water. In a typical case the normal reading was 66.6° S.R. When the pulp was steeped in .05% alum solution the reading was 57° S.R. This was not a wet beaten pulp however. With some wet beaten pulps the effect of steeping in alum is in the opposite direction. For instance, a certain pulp gave a reading of 90° S.R. in distilled water and 91.6° after being boiled with dilute alum solution and cooled before testing. This pulp was probably so shortfibred and finely beaten that a good deal of fine fibre escaped through the tester wire altogether in the first test, and was later coagulated by the alum boiling treatment and retained on the wire. This pulp gave a similar result when the

weight used was diminished so as to give a greater amount of fast draining water. For these reasons the Schopper-Riegler tester was only used as an instrument for rapidly characterising the drainage properties of the pulps used. This it does very well indeed in most cases.

13. Summary.

A brief summary, without discussion, is appended of the results of experiments on beaten cellulose suspensions.

(a) A Flow Tester is described for measuring the drainage properties of beaten cellulose suspensions. It is shown how the flow rate obeys Poiseuille's law within reasonably wide limits, and how it is possible to characterise each pulp by a flow-constant (F) so that results may be obtained which are independent of the weight of pulp, and the temperature of the water.

(b) It is shown how the method is applicable to the study of the properties of beaten cellulose suspensions in other liquids than water, and how dehydration phenomena in alcohol solutions become measurable.

(c) A whole range of ionic coagulation phenomena are discussed and it is shown that in general the cation alone is active. The dependence of ionic coagulation on the valency of the cation is shown. The adsorption of the cation by the cellulose is briefly discussed. Neither peptisation nor protection effects have been definitely established.

(d) A curious set of reversible coagulation phenomena are examined, which are caused by water at 70°C. and over. The instability of the flow-constant on prolonged steeping in water is shown.

(e) The lyotrope series of anions does not appear to be very important as regards the drainage properties of beaten cellulose suspensions. The effect of 'chemical hydrating' solutions such as concentrated $Ca(CNS)_2$, cuprammonium etc. has been studied, and a very free pulp was found to result after reversion and dilution.

(f) The dehydrating action of alcohol and alcohol-water mixtures has been examined. It is concluded that the ionic coagulation effect is nearly absent in concentrated alcohol, but is the same in 40% alcohol as in water. There does not seem to be any tannic acid dehydration effect.

(g) It is found that asbestos suspensions do not show any comparable dehydration effects in alcohol, or ionic coagulation effects in aqueous solution.

The general discussion on the above results is deferred until the end of the experimental part of the paper.

R E F E R E N C E S.

137 Pap.Fab. Festheft (1930) p.118.

138 Nakano, J.Cell.Inst.Tok. 6.89,106. (1930).

IX.
COHESION AND DENSITY OF BEATEN CELLULOSE.

The most important results of the beating operation are to be found in the strength properties of the beaten sheet. Experiments on aqueous suspensions of beaten fibres can only afford somewhat circumstantial and indirect evidence of these effects. The development of strength by the beating process has been very widely studied, and does not form the central topic of this part of the paper. Strength tests on beaten cellulose involve the whole technique of sheet-making, drying, conditioning and testing. It was considered therefore that it might be possible to test the beaten pulp without making it into sheets, and yet in such a way that its sheet-making properties might be predicted in advance. The effects of the beating operation have been shown to be exceedingly complex, but it has been suggested that the prominent characteristic of the paper-making fibres, and especially of the beaten fibres, is that property of surface cohesion which renders possible the formation of a strong sheet. It has been suggested that this is due to a colloidal surface film which is developed during beating by a process analogous to the imbibition of water by elastic gels.

If the analogy of the elastic gels is closely followed we might try to measure the water of imbibition by the method suggested by Strachan[36], i.e. the removal of the capillary water and the retention of the imbibition water under considerable mechanical pressure. The predominant feature of the swelling of elastic gels

in water is generally considered to be the contraction in the total volume of the system, owing to the penetration of the water into the intermicellar voids. Lastly the amount of 'bound' or 'imbibition' water might be measured by a process of negative adsorption such as has been used in certain physiological problems referred to in Part VI. The above three methods will be dealt with briefly from the experimental point of view in the present part of the paper, but it will be shown that they do not provide a suitable method of measurement of the degree of development of the colloidal surface film produced by beating.

The chief function of the film would appear to be the promotion of the bonding of the fibres to each other in the course of drying. The mechanism of such bonding must be the rendering available of the residual valencies by their temporary utilisation in the bonding of water molecules in the surface film. If this theory is correct, the development of strength qualities in the beaten sheet will at least partly depend on the development of the colloidal surface film during beating. If therefore a cake of wet, beaten fibres of random orientation be formed, this would contract during the drying process to a dense cake of cellulose, the ultimate density of which would approach the true density of the cellulose substance more or less in proportion to the degree of completeness with which the colloidal surface film had been formed in the course of beating. Owing to the composite and hollow nature of the fibres, the density of such a dried cake would never be as high as

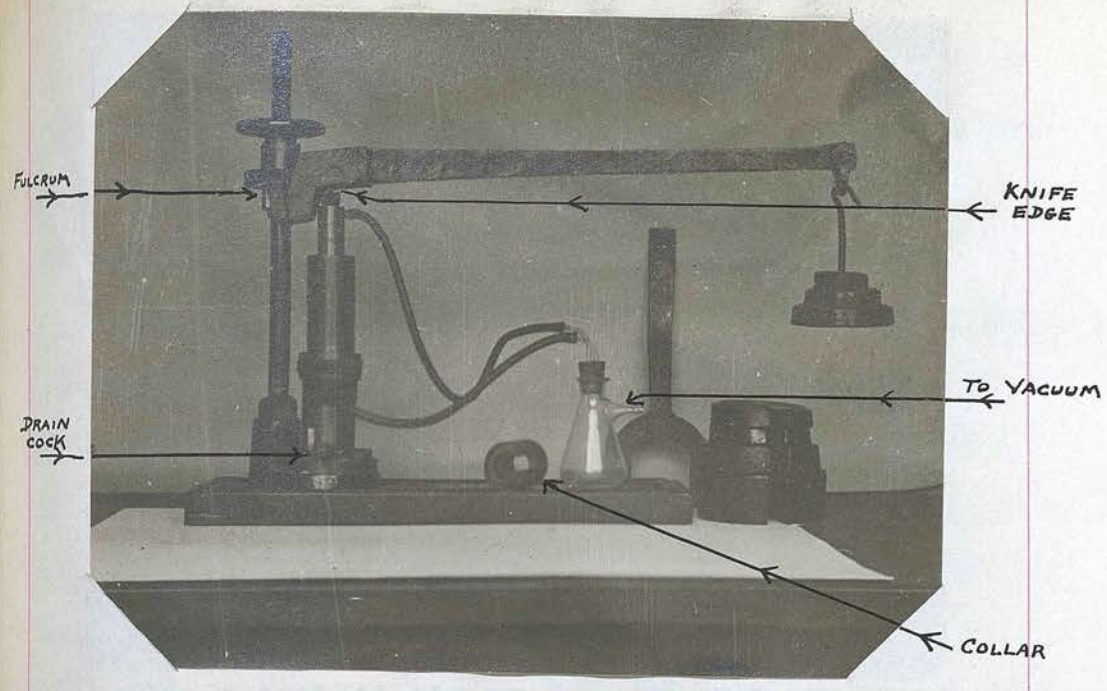
the true density of the cellulose substance. By a preliminary group of experiments it was found however that the range in the density of such cakes for different degrees of beating was very great, varying from 0.3 for unbeaten cakes to 1.25 for highly beaten cakes. For the experimental results to be comparable it was of course necessary to form the wet cakes under identical conditions for each experiment. For this purpose a press was necessary. The determination of density had to be performed by means of a mercury pyknometer. Drying conditions had to be standardised, and a scheme of experimental corrections introduced for accidental errors in the conditions of experiment. The same press could be utilised for the determination of imbibition water by the pressure method, and the cakes were well adapted for determining the apparent density and total volume contraction (if any) of the cakes in the wet condition. With such a material as fibrous cellulose it is clear that the air-space both within and between the fibres introduces great difficulties into the problem of the accurate determination of volumes, especially when the fibres are in contact with a non-wetting liquid such as mercury.

1. Outline of the Volume-Contraction or Cohesion Method.

It is clear that a method which depends on the accurate measure of volumes offers certain difficulties in the case of fibrous cellulose. It is necessary to arrange that the pressed cellulose cake shall be of simple shape and of small external surface compared to its

volume. In practice a short cylindrical cake has been chosen. The ultimate contraction of volume during drying will depend on the initial proportions of fibre and water in the pressed cake. Other causes of variation may be the manner of packing the wet fibre into the press cylinder, the rate of pressing and the rate of drying. Difficulty may be experienced owing to the lack of cohesion of the fibrous cake, causing development of cracks during drying, with the result that globules of mercury may enter and vitiate the measurements.

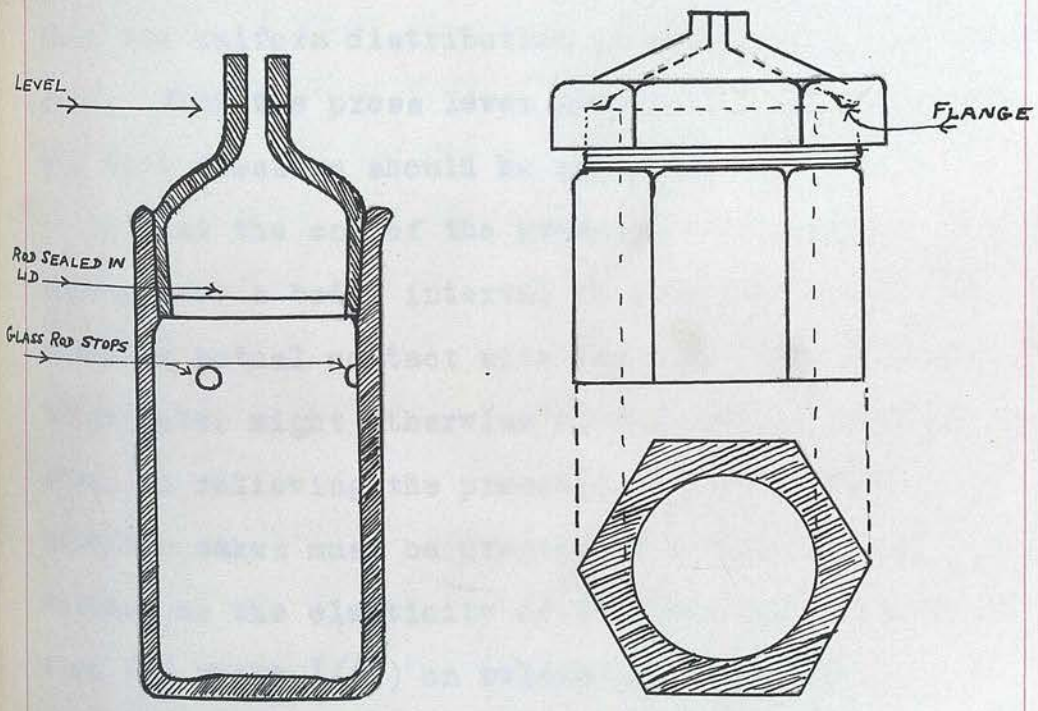
The press used is shown in the photograph. It is a simple weighted lever press with a hollow brass piston working accurately within a stout brass cylinder. Both below and above the pulp cake is a small disc of wire-cloth of fairly close mesh. Below the lower disc is a perforated brass plate. A similar brass plate screws flush into the lower part of the piston, and is connected by an inner tubular passage to an outer nozzle which may be connected by capillary tubing to a vacuum pump. In like manner the space below the lower perforated disc can be connected to the pump. The ratio of the lever arms is about 14 : 1, and it is easy to put on any pressure between 20 and 200 lbs per sq. in. The position of the lever is readily adjusted by screwing down the fulcrum bearing on the fixed upright. In practice it is usual to press to a definite volume, and for this purpose the hollow brass collar (lying loose in the photograph) is placed round the plunger and on the top of the cylinder. The knife edge of the lever



AUTHOR'S PULP CAKE PRESS

made by

Messrs John White and Son, Weighing Machine Makers,
Auchtermuchty, N.B.



Glass Steel

PYKNOMETERS (Natural size)

is fairly long, and its outer parts will then come to rest against the brass collar. To obtain satisfactory and uniform cakes the following details should be observed.

(a) The standard weight of dry fibre used has been fixed at 8gms. This should be in the form of a lump of wet pulp of total weight 45 - 50gms. This amount can be just squeezed into the press cylinder without any preliminary evacuation or pressing, and the resulting cake is thus better formed. It is advisable to eliminate entrained air as well as possible during the packing process.

(b) The pressing should not be too rapid. There is no harm in using suction to both top and bottom of the cake during the preliminary stages of pressing. This in inadvisable in the later stages as tending to prevent the uniform distribution of moisture in the pressed cake. When the press lever becomes nearly stationary the full pressure should be applied.

(c) At the end of the pressing it is good to apply suction for a brief interval in order to remove the water in actual contact with the pulp cake surface, which water might otherwise become reabsorbed into the cake, on relieving the pressure. Lightly beaten or unbeaten cakes must be pressed to a somewhat smaller volume, as the elasticity of the cake may cause expansion (of about 1/8") on release of pressure.

(d) The standard cylinder diameter is 1 inch. The standard pressed-cake volume has been fixed at 18cc, and the height of cake corresponding to this is

somewhat under 1½ inches.

(e) Drying is conducted for convenience and rapidity in an oven at 100 - 105°C. It is quite true that a very slow process of drying in a desiccator at room temperature gives a greater volume contraction, but reproducible results can be obtained by drying at the higher temperature. It is also the case that, for very well beaten cakes it is difficult to expel the last 1% of moisture, but it has been shown that the expulsion of this is not accompanied by any change of volume.

(f) Volume measurements are made in a small mercury pyknometer. For most experiments a glass vessel has been used with carefully ground in hollow stopper and capillary stopper neck. The cake is prevented from interfering with the stopper by three small pieces of glass rod fused to the inside of the pyknometer, against one or two of which the cake rests when the vessel has been filled with mercury. For a closer study of volume changes near the dry end of the drying process a small steel pyknometer has been used with screw-down lid resting against a broad smooth rim. The stopper of this bottle has also a narrow tube in the upper part. It has been found necessary to correct for temperature in the case of the glass pyknometer, but differently in the case of the steel pyknometer. The pyknometers are illustrated below the pulp press photograph.

It is clear that a measure of the cohesion property of the beaten pulp may be obtained either directly from the density of the resultant dried cake, or from the volume contraction during the drying process. The

relation of the two quantities is a simple one. In the case of a well beaten cake it is found from measurements of the density of the wet pressed cake that the apparent density of the cellulose is about 1.55. The volume of 8gms (standard fibre measure used) is therefore 5.16cc. The total volume being 18cc, it follows that 12.84 gms of water are present, and the weight of the wet cake is about 20.8gms.

If d, v are the density and volume of the dry cake, then $v = \frac{8}{d}$. The volume contraction ratio will be $\frac{18}{v} = \frac{9d}{4}$. In practice it is desirable to use such a measure of cohesion as will be fairly small for unbeaten pulp and practically zero for cakes of a material such as asbestos, where the surface cohesion property is negligible. Unity is therefore subtracted from the volume contraction ratio, and the difference is multiplied by 1000 to give a convenient number for recording purposes where the accuracy of measurement does not extend beyond the units digit. For example if $\underline{v}$ is found to be 6cc the contraction ratio becomes $\frac{18}{6} = 3$, and the cohesion number $(C_h) = 2000$. For unbeaten pulps $C_h = 180 - 200$. It is of course not possible to regulate matters so that the dry weight shall always be exactly 8gms, and still less possible to adjust the wet volume to 18cc. A simple correction formula has been worked out to deal with small deviations.

$$\text{Uncorrected } C_h = 1000\left(\frac{\text{wet vol}}{\text{dry vol}} - 1\right)$$

Assume that corr. C_h = uncorr. $C_h\left\{1 + x\left(\frac{\text{dry wt} \times 2.25}{\text{wet vol}} - 1\right)\right\}$

Normally of course $\frac{\text{Dry wt} \times 2.25}{\text{Wet vol}} = \frac{8 \times 2.25}{18} = 1.$

A good many experiments have been done with several pulps varying considerably in 'beating degree' and hence in shrinkage on drying. For any one pulp the values of

corrected $C_h = A + Bx$.

If M is the mean value of C_h

$\Sigma\{M - (A + Bx)\}^2$ should be a minimum. Of course in this case the value M is the mean of the true values of C_h, and therefore involves the unknown quantity $\underline{x}$. The equation can therefore be expressed

$\Sigma(C + Dx)^2$ must be a minimum. Hence by differentiation $\Sigma D(C + Dx) = 0$

$$x = -\frac{\Sigma CD}{\Sigma D^2}.$$

A measure of the possible accuracy of the volume contraction method was readily obtained during this investigation. A well ball-milled stock Cd was made by beating for 23 hours. Its wetness was 89° S.R. and its flow constant 44.9. Ten determinations of the cohesion number were made, and a value of $\underline{x}$ calculated as above by the method of least squares. Using all of these values the following results were obtained --

Mean of uncorrected C_h values	1734	mean deviation	12.5%
x = 1 corrected C_h mean	1790	-- --	5.0%
x = 1.5 -- -- C_h --	1817	-- --	2.6%

Neglecting the two values which were farthest from the standard conditions, the results were:-

Mean of uncorrected C_h values	1834,	mean deviation	8.1%
x = 1 corrected C_h mean	1828	-- --	3.5%
x = 1.4 -- -- C_h --	1826	-- --	2.6%

Similar values of x were found for the cases of lightly beaten pulps (where the correction required was

small) and two other cases. As a result x could be satisfactorily related to C_h according to an approximately linear law, as shown in the following table, which sums up the work done on this method of measurement till July 1927.

x	0.5	.6	.7	.8	.9	1.0	1.1	1.2	1.3	1.4	1.5
C_h	below 700	820	940	1060	1180	1300	1425	1550	1675	1800	2000

The process of arriving at the cohesion constant is in reality no more complicated than if the dry density had been chosen as the quantity to be measured. In the latter case a similar correction for variations in experimental conditions would have had to be introduced, and for the same reason. This method was chosen in order that it might be applicable over as wide a range of beating conditions as possible. For this reason the idea of pressing to equilibrium volume under a standard pressure was rejected. Equilibrium may not be reached for many days in some cases. It is clear that the present method is applicable to measurements where the fibres are wetted with some other liquid than water, and also to any material other than cellulose which can be pressed into a coherent cake.

2. Preparation and Purity of the Cellulose.

Except in the matter of some special experiments the fibrous cellulose used throughout the whole of the present investigation, including that used for the experiments on flow constants and sheet properties, has been substantially the same. A fair number of sheets of a typical easy bleaching sulphite wood pulp (spruce wood) were cut up into identical bundles of about 1 lb weight.

Bleaching was conducted in a small laboratory beater with 10% of bleaching powder calculated on the weight of the pulp. A second bleach was given after washing, using 20gms $KMnO_4$ per Kgm pulp (or .3% active oxygen). The pulp was washed with tap water and then treated with a solution of sodium sulphite acidified with acetic acid, in order to dissolve oxides of manganese and other basic constituents. Careful washing with distilled water followed, with intermediate concentration of the pulp in a flannel bag in a hand press. The last wash waters showed a pH value of 7.0. In certain cases the rosin was extracted from the dry pulp prior to bleaching, by means of warm industrial alcohol. Beating of the pulp took place in a pebble-loaded jar mill. The jars were of stoneware, and had a capacity of 4700cc. for a depth of 8½ inches. The cylindrical jars revolved about their axes in a framework, so that four jars could be beaten at a time. The speed of rotation was kept constant at 67 revolutions per minute. For producing a long-fibred, wet beaten pulp the following conditions are typical.

Use 60 gms air dry pulp (this treated pulp was usually preserved in a condition of 33% pulp, 67% water) with 1000 gms quartz pebbles (21 stones) and 1500cc. total distilled water. After beating for 60 hours the beating degree was 93.6° S.R. and the C_h value 1874. The initial tests on the pulp were 16.5° S.R., C_h = 185. By using less pulp and a heavier weight of pebbles results can be obtained much more quickly. Even with the above

quantities the beating degree will be found to be 85° S.R. after a quarter of the time. In 3 - 4 hours it is possible to beat to 40° S.R. with a C_h value of over 500.

The typical prepared but unbeaten pulp gave the following results, compared with the same pulp beaten for 48 hours to beating degree 95° S.R., C_h = 1900.

	Unbeaten	Beaten
Ash	0.49	2.67
Resin	1.20	Same probably
Copper number	2.27	2.03
α Cellulose number	84.72	Unfiltrable.

With such a well beaten pulp it was practically impossible to determine the α Cellulose number by the usual caustic soda method. The resulting swollen pulp could not be filtered. In the case of a more lightly beaten pulp however (C_h = 700) the α Cellulose number was found to be almost 84%, or only slightly less than for the unbeaten pulp. Several other determinations of copper number before and after beating were made, and it was concluded that there was no appreciable degradation of the cellulose during beating, for the purified type of pulp used in these experiments. It is nevertheless the case that very well beaten pulp cakes or sheets show much greater discoloration on drying than sheets made from the unbeaten pulp. If the beaten sheets or cakes are thoroughly washed in alcohol before drying the discoloration is avoided completely. This discoloration occurs whether the drying is at 15°C or 100°C. Careful experiment shows, however, that no error was introduced into the weighing of the dry cake

in this way. An appreciable error only occurred if the pulp had been wetted with a solution of a mineral acid, or of the hydrolysable salt of such an acid before drying. The increased ash content of the beaten pulp was due to insoluble clay constituents abraded from the surface of the jar mill. The original pulp ash was not quite insoluble in water. An experiment gave the following results. The ash was boiled up with 100cc of distilled water, and the cooled extract was tested for electrical conductivity. In the case of the ash from 4.44 gms dry unbeaten pulp the conductivity of the resultant solution was equivalent to what would have resulted from dissolving .0032 and .0036 gms respectively of calcium carbonate in the distilled water. The ash on the unbeaten pulp in this case amounted to 0.215%. In the case of the same pulp pebble-milled for 50 hours the ash amounted to 2.49%, but the conductivity was much lower, being equivalent only to .00065 gms of $CaCO_3$. The amount, in any case, is insufficient to interfere with flow-constant determinations, if indeed the calcium salt is not altogether firmly bound in presence of the fibre. For all experiments on cohesion numbers and sheet properties the ash is without effect of any kind.

3. Typical Results by the Cohesion Method.

A group of representative data will first be given for several typical beaten and unbeaten pulps. The data will include the cohesion number, the density of the dry cake, the density of the cellulose as calculated

from the weight and volume of the wet cake and the weight of the dry cake, and the cohesion number for the same pulp previously saturated with industrial alcohol before pressing. The ratio of cohesion number in water to that in alcohol will also be given. Comparative results on the same pulps with the Schopper-Riegler tester and the flow-meter are also included, all the experimental work having been done before May 1927, but the C_h values having been subsequently corrected according to the later method.

	No. of Pulp	A	B	C	D	E	F
a	Beating Degree °S.R.	16	54	79.5	53,6	80.4	89.0
b	Flow-Const. Water	?	1.81	13.33	3.02	24.5	44.9
c	-- -- alcohol	?	.415	1.57	.414	1.662	5.06
d	Ratio Faq/Falc	?	4.36	8.49	7.3	14.76	8.87
e	Density of dry cake	.483	.535	.649	.737	1.078	1.261
f	Apparent cellulose density	.894	1.11	1.33	1.46	1.57	1.55
g	Cohesion No. Water	176	277	511	579	1410	1826
h	-- -- alcohol	54.5	112	152	202	247	335
i	Ratio C_{haq}/C_{halc}.	3.23	2.47	3.36	2.87	5.71	5.45

Only rows c and h were done in industrial alcohol. All the other tests were done in water.

The pulps in the preceding table had undergone the following treatment.

A. Unbeaten standard pulp.

B. A mixed esparto and wood pulp beaten on the industrial scale for 4 hours so as to make a strong white paper.

C. An industrial beaten wood pulp, which had been

severely beaten with sharp tackle for 8 hours with the object of producing a short-fibred filler pulp for a paper impervious to air.

D. A lightly treated standard pulp, 16 hours in the pebble mill, 60 gms dry, 2000cc water, 1000 gms pebbles, (always 18 or 19 stones).

E. A similar case, but where 2000 gms pebbles were used for the same length of time.

F. 60 gms pulp, 2000cc water, 2500 gms pebbles, 22 hours. This is really about as lightly beaten as E, as the motion of the pebbles was impeded by their too great volume in the jar.

It is clear from the table that no great reliance can be placed on the flow-constant results as a measure of beating degree, nor on the Schopper-Riegler figures near 90°S.R. The dry cake density and C_h figures run parallel to each other, as is to be expected. The apparent cellulose density calculated from the wet cake data and the dry cake weight doesnot take any account of entrained air, nor of the ash content of the pulps after prolonged beating. As will be shown later, cohesion data in alcohol are liable to a considerable error due to cracks developing in the cakes. Also a considerable fall occurs as the alcohol concentration rises from 90 to 96%.

One further short table will be given showing the changes during the course of beating an esparto-wood paper.

Hours beaten	1	2	3	4	5
Beating degree °S.R.	23.5	32	44	47.5	54
Cohesion No. C_h	170	193	231	260	283
Density dry cake	.427	.472	.493	.520	.537

If the cohesion number is to be used as a recording constant for beaten pulp it must be remembered that the presence of mineral loading, such as clay, will lower the value of C_h, if the calculations are performed in such a way that the weight of the dry fibre cake includes that of the clay. If fibre weight only is used in the calculation there is very little diminution at all. If the cohesion test were used on the industrial scale, the easiest method of reckoning would be the first named. For an unbeaten pulp, with the 50% clay addition, C_h will fall from 190 to 130. In the case of the pulp F in the previous table the addition of 30% of clay lowers C_h from 1826 to 1087. It has been found that dilute solutions of electrolytes such as alum have no effect whatever on the value of C_h.

It is clear that the low values for the cellulose density, calculated from the volume of the wet cake, must be due to entrained air. Several experiments with relatively less beaten pulps have been done, the pulps being boiled under a vacuum and at atmospheric pressure for several hours, but the results have been largely negative. Neither has the value of C_h been materially altered by such treatment, nor by boiling in a very dilute $Al_2(SO_4)_3$ solution and subsequently cooling before testing. As might be expected therefore,

the C_h value of a pulp is unaltered by prolonged steeping in water. These conclusions have been completely established both for unbeaten and highly beaten pulps.

4. Dehydration in Alcohol, Asbestos Cake Contraction.

Alongside the tests which were done on the variation of the flow-constant in graded mixtures of alcohol and water, a series of measurements of cohesion numbers were also made on the same two pulps. The first pulp used, Da, was a long-fibred pulp made by pebble-milling 60gms of standard bleached pulp for 16 hours in 1500cc of distilled water with 1000gms pebbles. The other pulp, No.224, was beaten with 2000gms pebbles in 2000cc water for 24 hours. Hence the fibre length was a good deal shorter, and there was a larger proportion of fibre debris. The experiments on the alteration of flow and cohesion constants, with variation of the alcohol content of the suspension or wetting liquid, were all done about the same time in February 1928. The alcohol used was industrial alcohol (methylated), but the percentage alcohol recorded in the following tables is based on the analytical figures of the makers, the mixtures being all made up by weight.

Results on No.224 Pulp, beating degree 91°S.R.						
No. Experiment	224	241	242	243	244	245
% Alcohol	nil	nil	30	50	70	90
C_h corrected	1691	1653	1413	1433	884	386
Relative C_h	100		84,5	85,7	52.8	23.1

As usual the cakes were dried at 105°C, and with this short-fibred pulp the partially and completely dehydrated cakes fissured somewhat badly on drying,

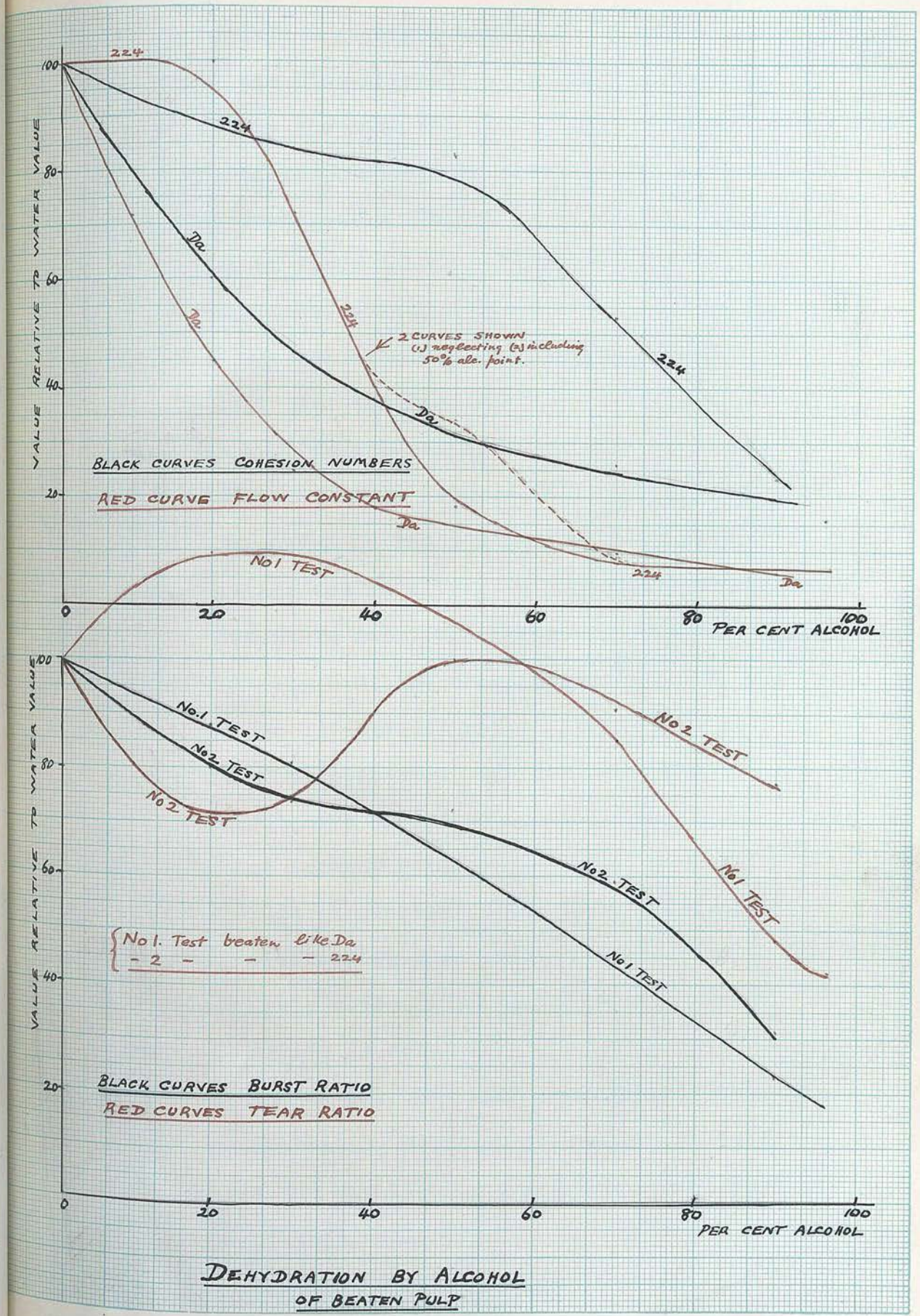
resulting in errors in the measurements. The final figure can also be expressed. C_h water/$C_h$alcohol = 4.33, in line with the results previously quoted.

Results on Da pulp, beating degree 87°S.R.

Here duplicate determinations were made in all cases, and percentage deviations from the mean are therefore available as measures of accuracy of the determinations. The 96% alcohol was made by redistilling the industrial alcohol twice over quicklime. The density was .8033 at 18°C.

Expt. No.	Alc. %	Density dry cake	Mean	Devn. %	Corr. C_h	Mean	Devn. %	Relve. C_h
249	0	1.005	.994	1.1	1217	1236	1.5	100
250	0	.983			1255			
256	10	.869	.874	0.6	965	986	2.1	79.8
257	10	.879			1007			
253	20	.762	.748	2.0	754	736	2.6	59.6
258	20	.733			716			
252	40	,618	- -	- -	470	- -	- -	38.0
254	50	.595	.605	1.6	370	386	4.1	31.2
261	50	.615			402			
251	71	.554	- -	- -	322	- -	- -	26.0
248	90	.545	.525	3.8	277	243	13.6	19.7
260	90	.506			210			
255	96	.506	.500	1.2	192	193.5	0.7	15.7
259	96	.493			195			

The ratio $C_h$water/$C_h$alcohol works out at 5.09. The results of both flow and cohesion tests on the above pulps are shown in the accompanying graph. Da pulp



DEHYDRATION BY ALCOHOL
OF BEATEN PULP

gives a fairly uniform curve for both properties, although a reasonably complete dehydration is achieved in the case of the flow-constant at a lower percentage of alcohol than is the case for the C_h number. Da is a typical long-fibred, wet-beaten purified sulphite pulp which has been gently treated so as not to produce much in the way of fibre debris. The case of pulp 224 is far otherwise. The cohesion tests are so irregular that they were classed as due to experimental error, until it was seen that the flow-constant data were equally anomalous. Unfortunately there was not enough of the pulp left over to go into the matter again and, since that date, owing to the pressure of other work, the opportunity has not recurred. It can only be suggested here, that where there is considerable destruction of fibre during beating, the whole fibres and the debris will behave differently under the partial dehydrating effect of alcohol-water mixtures, so that a different form of curve may be expected. The phenomenon is worthy of further study. It should be added here that, although it has been shown that the alcohol dehydration effect between 100% water and 90% alcohol is almost completely reversible, as far as the ultimate contraction on drying is concerned, yet in all the above experiments the pulp has been successively washed with gradually increasing percentages of alcohol in the mixture, so that the equilibrium has always been approached from the water side only.

A series of parallel experiments was conducted in January 1929, in which the beating in the pebble mill

was conducted in water, 90% alcohol and a light petrol (density .742) respectively.

The same purified bleached sulphite pulp G was used in all cases. Where the beating was conducted in another liquid than water the pulp was carefully wetted with this liquid before beating. This was easy in the case of industrial alcohol. In the case of petrol, the moist (water wetted) pulp was successively washed with stronger alcohol solutions up to 96% and with acetone. Finally the latter was displaced by petrol. The petrol had been dehydrated over quicklime. In each case 50gms of dry pulp was beaten in 1500cc of liquid using 2000gms of pebbles and beating for 6 hours.

It is of course obvious that it is impossible to ensure that the mechanical effect of the beating should be the same in each case. The density and viscosity of the liquids were different. The surface tension being small in the case of alcohol and petrol, the liquid films would be more easily broken, and there would be less air-cushioning effect. An examination of the beaten fibre showed that, particularly in the case of petrol, the fibre tended to agglomerate into lumps rather than to distribute itself uniformly in the liquid, as in the case of water. This would be a natural result of the lyophobic behaviour of cellulose fibres in a hydrocarbon liquid.

After beating, the several pulps were tested in their own liquids for Schopper-Riegler beating degree and cohesion number. Sheets were also made for strength tests. The Schopper-Riegler and cohesion tests were

also repeated after replacing the alcohol and petrol by water, and sheet tests were also done in water for the alcohol and petrol beaten pulps. The results are given briefly in the following tables.

a. Schopper-Riegler tests.

Pulp	Beaten in	Tested in Petrol °S.R.	Alcohol °S.R.	Water °S.R.
Ga	Water		43.2	68.6
Gb	Petrol	14.5		22.0
Gc	Alcohol		27.4	35.0

b. Cohesion tests.

Pulp	Beaten in	Tested in Petrol C_h	Petrol Dry density	Alcohol C_h	Alcohol Dry density	Water C_h	Water Dry density
Ga	Water			213	.534	1364	1.066
Gb	Petrol	85.0	.504			421	.560
Gc	Alcohol			144	.480	431	.624

The strength tests on the sheets will be discussed in the last experimental part of this paper. They accord fairly well with the cohesion number. No flow tests were done. It must be added that it is not at all shown to be impossible to get a fair beating effect in a hydrocarbon liquid. It is however necessary to study the mechanical conditions carefully so as not to damage the fibres unduly. The optimum development of strength characteristics for a given pulp can probably be arrived at only if the beating is done in water, but careful treatment in 90% alcohol can be made to give a quite satisfactory result. Petrol is not nearly so satisfactory. It is probably the case that the last

5 - 10% of water in solution in the alcohol is able to develop the hydrated surface film on the fibres to a small extent, and to promote the bonding of the fibres during the sheet-making and the cohesion test.

A series of experiments was done on beaten asbestos during October 1927, at the same time as the flow tests were done on this material. As was expected the cohesion numbers were very low. In the first and almost unbeaten tests the C_h numbers were actually negative both in water and alcohol. This means that a very slow recovery took place during drying from the compression process of the cake preparation. This result was only obtained however when the cake was considerably more compressed than according to the standard method. In like circumstances cellulose cakes give a lesser cohesion number than usual, but always a positive one.

The records of the beating tests were as follows:-

	Time beaten	Gms pebbles	cc. water	Asbestos
1st Beating	16 hours	1000	2000	50gms
2nd - - -	16 hours	2000	2000	- -
3rd - - -	50 hours	750	1500	- -

Thus the second beating was intended to be drastic, and the third to produce a very gentle effect. The cakes for the cohesion tests all dried well without developing any cracks. Owing to the very small C_h values obtained, the deviations were relatively more considerable.

The following table shows the results of the cohesion tests.

	C_h water	C_h alcohol
First beating	142	- 15
Second beating	225	- 2
Third beating	221	- 35

One final experiment was performed, adding a sol of gelatine to the beaten asbestos in order to simulate the presumed colloidal surface film on the cellulose fibres. The asbestos used was from the third beaten lot. A 2% sol of gelatine was used, and 8gms of asbestos took up about 40gms of sol before being pressed. After pressing the wet asbestos cake weighed 21gms, so that 0.26gms gelatine remained in the cake. The C_h value became 231. The experiment was unsuccessful. A similar experiment with a very slightly beaten cellulose pulp cake was equally without effect, except that the C_h value actually decreased to some extent.

The experiments with beaten asbestos show very well just how much of the volume contraction on drying can be properly attributed to the surface-tension of the liquid, and how much is due to the fibre-fibre bonding in the case of cellulose. By comparison with the previous experiments, where beating was conducted in petrol, it is seen that there is very little fibre-fibre bonding in a hydrocarbon solvent, and considerably more in a 90% alcohol. Nakano's experiments on sheet formation with asbestos may be recalled, in which he obtains mechanical felting but free slippage of the fibres over each other.

5. Volume-Weight Relations during the Drying Process.

The immense difference in the volume contraction on drying of beaten and unbeaten cellulose fibre cakes naturally suggested that the close study of the whole drying process from this standpoint might reveal some discontinuity, indicative of the relative amounts of 'free' and 'bound' water associated with the beaten fibre. It was not intended to follow the 'rate of evaporation' at different stages of drying as in the case of Rowe's work(108), but simply the volume and weight changes of the cake. The first experiments were done in December 1928 on a pulp Fb, 50gms unbeaten dry pulp being pebble-milled for 48 hours in 1500cc water and 1000gms pebbles to 95.1°S.R.'beating degree'. This pulp was also used to measure the strength properties of sheets made in various ways with several liquids. Successive measurements of weight and volume were made during the drying process, (a) drying in the oven at 100 - 105°C, (b) drying down to 7% moisture content at room temperature in a desiccator and finishing in the oven, (c) drying a cake made in industrial alcohol in the desiccator and finishing in the oven. In all cases the graph connecting $\frac{\text{wet}}{\text{dry}}$ volume with $\frac{\text{wet}}{\text{dry}}$ weight turned out to be a straight line for all points studied during the drying process, except those very near to the dry end. It was very noticeable that if C_h numbers were calculated, using of course the first and last measurements, these numbers were higher for desiccator than for oven dried cakes.

	Water made cakes			Alcohol	Petrol
	desiccator		oven	desiccator	oven
Dry density	1.363	1.338	1.291	.734	.610
C_h	2067	2013	1900	644	428

Thus slow drying favours cohesion of cake. It has not been deemed necessary to give the complete data for these tests, for a more comprehensive series was started in February 1929 with the object of establishing the conclusions more carefully, and checking the non-linear part of the curves near the dry point of the cake. One other observation was made to the effect that the apparent density of the cake showed a maximum before the dry point was reached, but this was somewhat irregular. The only explanations could be, either that the last traces of moisture were expelled without decrease in volume, or that an actual expansion occurred at this point.

In any case it was decided to examine the weight-volume relationships during the drying of 8 cakes made from 3 different pulps, all extremely well beaten but of different fibre length. The starting point was the standard pressed cake of approximately 18cc volume. The method of oven drying was deemed to be too rapid, and the method followed was to dry the cakes side by side standing on a wire grid in the open air of the laboratory until such drying became too slow. The process was then continued in a desiccator over conc. H_2SO_4, and the last portions of water were removed in an oven at 100° -105°C. The drying process was now very slow indeed for well beaten cakes, the moisture content at

this stage being only about 7%. The cakes were transferred to the desiccator after 20 days, to the oven after 84 days, and were considered to be finally dry after 185 days from the start of the experiment. At intervals the weights of the cakes were determined and their volumes found from measurements in the mercury pyknometer. Owing to the large initial size of the cakes the glass pyknometer was used to begin with. At a certain stage of drying the steel pyknometer was used for all measurements. In the case of the glass pyknometer a standard scale of correction for temperature was used for the weight of the vessel completely filled with mercury. At 15.8°C the full weight was 672.0gms and there was 0.1gm increase for each degree of temperature lowering. For the steel pyknometer it turned out to be unnecessary to correct for this. In each case however the weight of mercury displaced by the pulp cake was corrected for variation of mercury density with temperature. As the volumes of the dry cakes were often as low as 5.6cc, it is clear that the error in the volume measurements was greater in this region. It is doubtful if the accuracy of measurement on such a volume makes the value of the second place of decimals perfectly certain, but in the calculations three places were retained. The steel pyknometer weighed 366.57gms empty and 443.2 full. Weighings were conducted to .05 gm. accuracy only. This procedure has been described because it is the same which has been used throughout for the determination of C_h numbers. Greater accuracy would have been misplaced, because of errors which are

bound to occur where a water-wetted cake meets a glass surface at an acute angle, and the great surface tensionof the mercury and its small wetting capacity combine to leave small voids. The good agreement of results shows however that this error could not have been at all considerable.

The following were the pulps used:-

Fd 75gms fibre beaten with 1500cc water and 1000gms pebbles 100 hours 93.7°S.R., C_h = 1644, long-fibred, for Nos. 292, 293, 300.

Fe 50gms fibre, 1500cc water, 1000gms pebbles, 100 hours, 95.1°S.R., C_h = 1718, shorter-fibred, used for Nos. 295, 296, 301.

Ge 1000gms fibre beaten in laboratory model beater 25 hours, well cut up, 86°S.R., C_h = 1614, short-fibred, used for Nos. 298, 299.

The results of the drying process are shown in the following table. The upper figures in each row represent the weight ratios, and the lower the volume ratios. These quantities are -

(Upper row ($\frac{\text{wet}}{\text{dry}}$ weight - 1)1000

(Lower row corresponding quantity for volume.

Notes on the Table.

(a) The dry weight basis of the calculations is the dry weight after 185 days drying. There was no volume change between 171 and 185 days. The dry weights were still diminishing slightly; e.g. No.292 fell from 7.994 gms at 171 days to 7.977 gms at 185 days.

(b) No set of complete figures of weight and volume measurements has been given. It was felt to be desirable

Days	Fd			Fe			Ge	
	292	293	300	295	296	301	298	299
0	1680 2303	1723 2259	1961 2720	1689 2312	1783 2369	1799 2394	1658 2213	1738 2335
1	1094 1465	1156 1526	1309 1781	1137 1521	1161 1505	1154 1497	1098 1443	1149 1517
2	645 824.4	686 861	785.5 1027	691.4 874.5	661.4 796.4	655.1 802.1	634 775.1	675.5 848.7
3	330 381.8	352 391.6	387 452.2	352.3 396.7	335.2 377.7	328.5 368.9	327.2 356.7	340.2 380.4
5	216.6 236.0	226.1 231.4	225.5 246.3	223.2 246.3	215.6 221.4	205.6 217.0	213.2 217.1	213.0 212.4
6	190.3 197.0	199.4 198.7	198.2 208.2	196.0 194.7	189.2 185.8	179.7 176.5	189.0 183.2	187.4 180.6
8	163.9 175.2	171.7 173.1	170.1 171.6	168.0 167.8	162.0 165.0	152.4 160.7	163.3 160.4	161.6 149.5
12	138.8 147.0	144.7 143.4	143.7 145.0	140.6 135.4	135.1 132.6	127.4 131.4	138.1 133.3	137.0 129.3
20	117.0 118.5	122.3 115.0	121.6 112.9	118.3 115.7	113.0 110.1	105.4 106.2	117.0 102.5	115.6 101.3
28	101.4 99.3	106.0 94.4	105.5 92.7	99.7 92.6	95.9 105.5	83.7 85.1	98.5 85.0	97.0 83.5
55	84.0 70.1	89.0 78.0	88.4 81.3	81.0 70.1	78.6 71.8	64.0 63.3	80.9 64.0	79.4 62.2
84	76.6 60.8	81.0 73.6	81.0 73.5	71.4 62.3	71.2 74.8	56.1 59.8	74.0 53.0	71.8 60.1
93	35.1 20.7	39.2 16.8	36.0 14.6	26.2 11.7	24.5 18.4	14.0 17.4	31.4 15.7	27.1 12.9
112	18.5 1.8	20.5 7.2	19.2 4.9	13.6 4.2	12.0 8.2	5.9 2.4	19.4 11.3	15.7 8.4
140	5.8 4.6	5.6 3.1	6.8 5.1	4.2 -ve	3.8 5.9	2.4 -ve	7.1 8.5	4.8 3.3
171	2.1 0.0	2.2 0.0	2.4 0.0	1.0 0.0	1.0 0.0	0.7 0.0	2.1 0.0	1.3 0.0

to vary the volumes of the wet cakes somewhat, to see if similar drying curves were obtained. This proved to be the case. Wet cake volumes varied from 18.15 to

19.46cc, and final dry volumes from 5.23 to 5.66cc. Final weights varied from 7.51 to 8.08gms.

(c) Of course it is quite clear that if a straight line is obtained by graphing wet/dry weight against wet/dry volume a straight line would also be obtained by graphing corresponding figures for weight and volume against each other direct. But the lines would not be the same for different cakes of the same pulp, and there would be no common origin for all the graphs drawn. As it was expected that all the lines would converge to such an origin, the above method of presentation of results has been preferred.

(d) The figures (not those quoted but the working figures) enable one to calculate corrected values for C_h in each case. These are quoted here as a measure of the accuracy of the method for determining such cohesion numbers. (Not oven dried results of course)

	C_h number	mean	deviation%	oven dried
Pulp Fd	(No. 292 2215.2) (No. 293 2184.2) (No. 300 2146.0)	2182	1.1	1644
Pulp Fe	(No. 295 2201.3) (No. 296 2112.4) (No. 301 2088.1)	2134	2.1	1718
Pulp Ge	(No. 298 2151.8) (No. 299 2145.0)	2148	0.1	1614

The merits and deficiencies of the method are thus well shown and the need for identical drying conditions.

(e) For all the eight cakes on which measurements were made graphs have been drawn. The quantities to be plotted are as follows:-

$$y = (\text{wet/dry weight} - 1)100$$

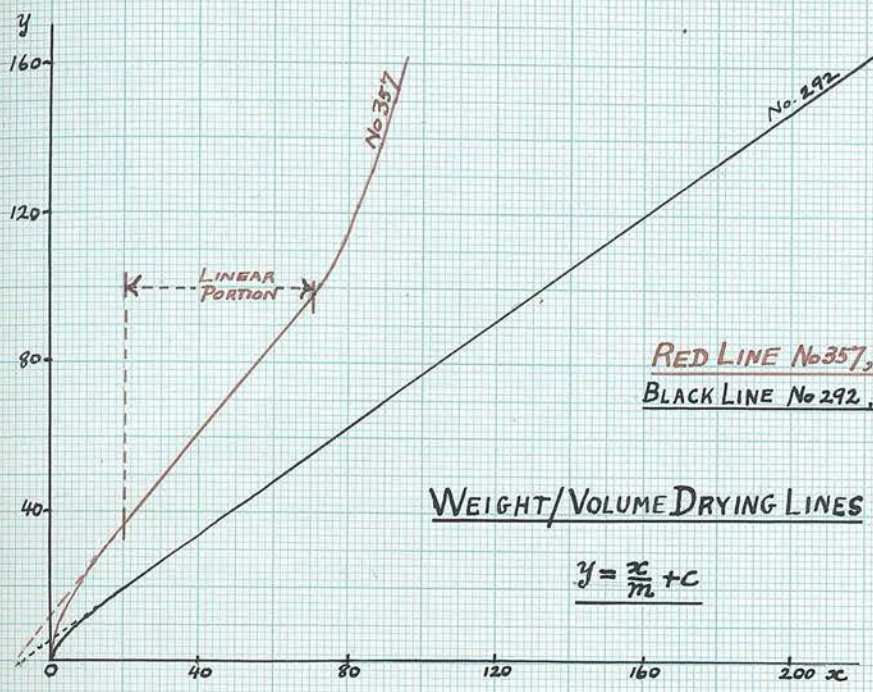
$$x = (\text{wet/dry volume} - 1)100$$

All the graphs are identical for practical purposes, and only one is shown on the next page. For values of x greater than 20 the graphs are straight lines, and the divergence of individual measurements from the line is very small. If this linear portion be produced to meet the y axis it will do so above the origin, and the intercept will be a measure of the percentage of water which can be held by the cellulose without subsequent volume contraction on drying. Naturally there will be a hysteresis effect, but the rewetting of dried cakes is a phenomenon which has not yet been studied from this point of view. The curve near the origin will probably be smooth, although the experimental results are irregular in that region. The perfect curve would probably reach the origin and be tangential to the y axis at the origin. The behaviour of the pulp can be characterised by the equation of the straight line portion - $y = \frac{x}{m} + c$.

The values of m and c are obtainable from the graph, or alternatively by the method of least squares from the coordinates of the first 5 or 6 points on the line starting from the wet end. Both methods have been used and the results, including the dry density of the final cake produced are given in the following table:-

(See next page)

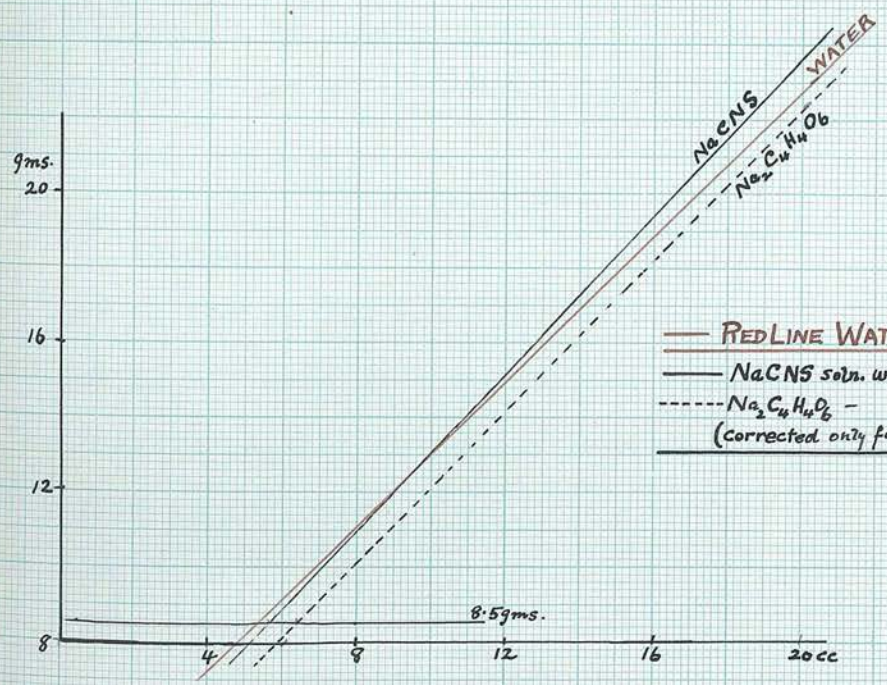
The results show fairly good agreement. It was therefore decided to repeat the experiments with pulps which were beaten to a less degree, and lastly to study very little beaten and unbeaten pulps.



RED LINE No 357, 36°S.R.
BLACK LINE No 292, 93·7°S.R.

WEIGHT/VOLUME DRYING LINES

$$y = \frac{x}{m} + C$$



— RED LINE WATER-WETTED
—— NaCNS soln. wetted
------ $Na_2C_4H_4O_6$ – –
(corrected only for salt weight)

LYOTROPE SERIES SALT EFFECT
DRYING LINE

cf. p176

	Graphically		Calculated		Dry
	m	c	m	c	density
No 292	1.407	6.20	1.416	5.74	1.433
-- 293	1.372	6.20	1.360	5.59	1.418
-- 300	1.426	5.80	1.403	4.59	1.435
Mean Fd	1.402	6.07	1.393	5.31	1.429
No 295	1.413	6.60	1.417	6.25	1.428
- 296	1.380	7.05	1.375	6.45	1.396
- 301	1.375	6.00	1.371	5.84	1.388
Mean Fe	1.389	6.55	1.388	6.18	1.404
No 298	1.389	6.90	1.393	6.83	1.403
-- 299	1.395	6.15	1.396	6.46	1.407
Mean Ge	1.392	6.52	1.395	6.64	1.405

In the intermediate category were the following:

No 359 Beaten 8 hours, with 1000gms pebbles in 1000cc water, 40gms pulp.

No 360 Beaten 5½ hours under same conditions.

No 361 Beaten in larger jars.

No 362 Beaten in laboratory beater for 3 hours.

In the lightly or unbeaten category were

No 355 Unbeaten pulp

" 356 Unbeaten pulp boiled in water 40 minutes to deaerate.

" 357 Beaten as 359 but for 3 hours only.

" 358 As 357 deaerated by boiling in water.

The results on the linear portions of the drying curves were as follows:-

No	Wetness °S.R.	m	c	Dry density	Apparent Cellulose density
355		.833	13	.742	1.036
356		.833	13	.712	1.017
357	36	.816	12	.811	1.300
358		.833	14	.819	1.308
362	43	.720	10	.745	1.234
361	51	1.06	11	1.078	1.535
360	60	1.15	10	1.153	1.538
359	82	1.35	10	1.362	1.591

Notes on preceding table.

(a) It is clear that it is not possible to deaerate the fibres by boiling in water, as the last column which gives the apparent cellulose density as calculated from wet cake volume and weight and dry cake weight is very low.

(b) The higher values of c cannot be held to show that unbeaten or lightly beaten pulp can hold a greater amount of water as a closely bound adsorption layer than very well beaten pulp. It is clear that in this case the less perfect bonding of the fibres permits of the replacement of the last 10% of water by air without volume change. It would only be in the case of perfect fibre-fibre bonding that the value of c could be held to represent the amount of the bound adsorption layer.

(c) The value of m is seen to be a good measure of cohesion. This is clear from the equations defining C_h and m, provided that the linear portion of the graph covers the standard range of the cohesion determination.

Let W, w be wet and dry weights,
V, v - - - - volumes.

For well beaten pulp the apparent cellulose density = 1.6 approx.

Hence $y = (\frac{W}{w} - 1)100 = (\frac{21}{8} - 1)100$

$x = (\frac{V}{v} - 1)100 = (\frac{18}{v} - 1)100 = C_h/10$

Hence $C_h = 1560m$ (putting $c = 6$)

(d) This method of calculation is not valid for nearly unbeaten cakes, as it has been found that the linear portion of the graph in this case only extends between values of W/w from 1.2 to 1.7. Above 1.7 the weight of the wet cake decreases with a lesser decrease in volume.

(See unbeaten drying curve p. 170A)

At standard wet cake conditions for unbeaten pulp W/w = 2.25 or so.

(e) In the experiments 355 - 362 inclusive only six pairs of values of weight and volume were measured, the first five in order to determine the graph down to a weight ratio of 1.25 or so, being made after room temperature drying in the open air of the laboratory at 13 - 16°C and then in a desiccator. For the last measurement oven drying at 105°C for 72 hours was employed. Trouble due to fissuring in the unbeaten cakes was experienced to some extent.

(f) It was clearly not practicable to start with a W/w ratio much greater than 2.25. The cakes would have been less coherent. A well beaten cylindrical wet cake does not preserve its shape on drying but develops a waist. The following table shows the changes in linear dimensions.

$\frac{W}{w}$ ratio	Height	Diameter max.	Diameter min.
2.63	192	128	128
1.70	144	120	104
1.18	116	106	97
1.01	109	104	91

It is thus impossible to prevent a stratified arrangement of fibres in a pressed cake, and the above measurements give an appropriate idea of the different behaviour of the fibres in the long and cross directions.

6. Effect of Steeping in Salt Solutions.

etc. on C_h number.

The somewhat inconclusive results obtained by the flow-meter method on the effect of steeping pulp in certain salt solutions rendered it desirable to study

the matter by the cohesion method. The experiments were done in the summer of 1927 and the pulps were exposed to the steeping treatment for 6 weeks at least. Experiments were done on a lightly, and on a very well beaten pulp. Where the steeping took place in acid or strong salt solutions the pulp was well washed before the cohesion test was made. The results in all cases were rather negative, although there was general evidence of a slight fall in C_h number with lapse of time. The results for the well beaten pulp alone are quoted here, as they show more variation. This pulp was numbered Cd and was also used for standardising the cohesion method. (see p.149) All figures quoted are corrected C_h numbers.

(a) Control tests before steeping the other samples.

Untreated pulp 1826 (average of several tests)

Steeped in $\frac{m}{1000}$ $Al_2(SO_4)_3$ solution 1774

" - - - $\frac{3m}{2}$ NaCNS - - - 1771

(b) Stored 6 weeks moist 1638, 1735

Boiled, $\frac{m}{1000}$ $Al_2(SO_4)_3$ solution, stored 1634

Steeped, - - - - - - - - 1642

Boiled, distilled water and stored 1694

(c) Steeped in a buffer solution of mixed m/15 solutions of $Na_2H\ PO_4$ and KH_2PO_4 for 8 or 9 weeks. The pH value of the solution was varied as follows:-

pH	8.1	7.7	7.17	5.9	5.2
C_h	1681	1637	1847	1596	1711

(d) Steeped in solutions of lyotrope series salts

2M NaCNS C_h = 1640

2M $NaNO_3$ 1727

2M	NaCl	C_h = 1700
2M	$Na_2C_4H_4O_6$	- 1786
2M	Neutral sodium citrate	1659
(e)	Steeped in n/50 HCl	C_h = 1687
- - -	- n/50 NaOH	- 1710

It was recognised that the cohesion properties of a beaten pulp remained unchanged by most steeping treatments, yet there is a distinct possibility that if the reagents are present during the beating process the rate of developing cohesion properties might be accelerated or repressed. It has been found to be difficult to repeat pebble-mill treatments with great accuracy, without treating several samples of pulp for each test, and it has not proved possible to find the time to carry out this particular investigation.

On the completion of the final series of tests on the volume-weight drying curves of different pulp cakes it was seen to be possible to estimate the cohesion number of a pulp without completely drying the cake, by merely determining 2 or 3 points on the straight line portion of the drying curve. Of course a knowledge of the dry weight of the cake is nesessary, but this is obtainable from a duplicate sample. The value of c on the standard drying curve varies little and a mean value can be assumed for a particular pulp. Thus it is possible to conduct measurements during the partial drying of a pulp cake soaked in various salt solutions. The first series of experiments was done on a pulp soaked in water, in m/2Na_2SO_4 solution, and in m/2NaCNS solution. The drying at room temperature was continued until the average salt concentration in the cakes had

doubled itself. The results were not very satisfactory. A second set of experiments were done on pulp M5 beaten to 93.6°S.R. and with C_h value 1874. The comparison solutions were m/2 NaCNS solution and m/2 neutral $Na_2C_4H_4O_6$ solution. With such a well beaten pulp it was concluded that the value of c (see equation p.170) might be taken as 6%. Weight, volume lines were plotted from 4 points, so that the lowest weight was not under 11gms (dry weight = 8gms). The points were fairly collinear and the line was projected back to cut the weight abscissa of 8.5gms $=(\frac{c}{100}+1)$ dry weight. The volume at this point was assumed to be the dry volume of the cake, and the cohesion number was easily calculated from the formula

$$C_h = (\frac{18}{v} - 1)1000$$

Some difficulty was experienced in the case of such strong salt solutions, whether it was advisable to correct the measured weights and volumes for the weight and volume of salt present. One such graph is shown on the foregoing page. (170A) It is remarkable how well the points fall on a straight line, (with the exception of those which are at or below 11gms weight), in all 3 cases. The practice has been to correct only for the weight, and not the volume of salt present in the cake. The results are as follows:-

	v	C_h
Cake in water	5.35	2360
- - NaCNS solution	5.65	2190
- - $Na_2C_4H_4O_6$ solution	6.4	1810

The result cannot be said to be very significant as it

is doubtful if correcting for the weight and not the volume of the salt is justified. If both are taken into account the results are identical for both salt solutions and water. If no corrections are made at all the thiocyanate C_h number becomes 2530, and the tartrate number 2460. The method is incapable of a refinement necessary to show with certainty anything less than fairly considerable differences of behaviour. It is possible to calculate C_h directly from the coordinates of two points on the drying curve, but the accuracy of the measurements does not justify the application of such a method.

7. Direct Determination of 'Bound' Water by Pressure Method.

Strachan[36] has suggested that the water of imbibition of beaten pulp can be measured directly by pressing the pulp under a suitable pressure to an equilibrium water content, provided that the pressure be greater than 10 lbs per square inch. The trouble is all in arriving at an equilibrium state. The author's pulp press was designed especially to prevent the reentry of expressed water into the pulp cake on releasing the pressure, and to preserve the minimum external surface of the cake. This means that the duration of the pressing operation is greatly increased for very well beaten pulps. The author has tried various pressures but considers that, as the object of the test is to remove all the free capillary water, it is better to use a fairly high pressure. The lever press used could be worked at 200 lbs per square inch, and this pressure was used through-

out. Very well beaten cakes took fully 14 days to attain equilibrium under this pressure. During all this time no suction was applied to the press. Just before removing the cakes suction was applied for 1 to 2 minutes to remove any water in the perforated plates below and above the cake. It was easy to see when equilibrium was attained, as the lever had a ratio of about 14 : 1, and a pointed rod could be set up in a retort stand to make contact with the outer end of the lever. Thus a movement of less than 1mm a day was very obvious, and this meant only 0.007mm on a cake about 26mm thick. Unbeaten cakes reached equilibrium in under three days, but a check test was done over 2 weeks to show that the loss of weight of the cake by evaporation inside the close-fitting press was altogether negligible. This proved to be so. In each case 8gms dry fibre was used.

The first accurate experiments were done in July 1927. The unbeaten pulp cake gave a ratio of wet to dry weight of 1.890. The well beaten pulp Cd (used for standardising the cohesion method, see p. 149) was in one case allowed to remain 4 weeks in the press. The final ratio was 2.093. As this was an extremely wet beaten pulp, it was clear that the method failed altogether to discriminate between pulps of moderately different beating degree. An experiment was done on beaten asbestos. In this case equilibrium was attained very rapidly and the corresponding ratio was 1.731. It is fairly clear therefore that most of the water that remains after pressing the unbeaten pulp is free capillary water, and as the capillaries of the beaten cake

will be finer, it is improbable that the pressure method is capable of giving any indication whatever of water which may be 'bound' in the colloidal surface film.

It appeared desirable to test the matter again at a higher temperature. Again a very wet beaten pulp M5 was used, which had a cohesion number of 1874, and a beating degree number of 93.6°S.R. The test at laboratory temperature took ten days, the mean temperature being 18.5°C. The weight ratio was 2.184. The high temperature was arranged by removing the press to a warm situation below a heat insulated tank containing a hot liquid. Equilibrium was attained in a week. Temperature readings were taken every 4 hours during that time by a workman on duty near by. The mean temperature was 34.6°C, and the extremes 42.4°C and 28.4°C. The weight ratio was 2.127. There is therefore no appreciable change due to temperature in the retention of capillary water by the cake.

8. Determination of Bound Water by a Negative Adsorption Method.

In Dec. 1930 and Jan. 1931 a number of experiments were done on the lines of the methods described in part VI p. 85 of this paper. It was intended to find out whether in a mixture of beaten or unbeaten fibres with an aqueous solution the solvent was shared out between the solute and the cellulose. Parallel experiments were done on an unbeaten and on an extremely well beaten pulp. Three solutes were chosen - sodium chloride, sucrose and phenol. Remembering the adsorption properties of cellulose fibres, especially beaten cellulose, it was

decided to usefairly small quantities of fairly concentrated solutions. Thus the solution strengths ranged from 11 to 16%. The solutes were determined as simply as possible after filtering clear through a cake of the cellulose itself on a Buchner funnel. Thus the NaCl was determined by evaporating the solution to dryness, the sucrose similarly but in vacuo, and the phenol by an iodometric method. In each case several experiments were performed, and in the case of the unbeaten pulp the equilibrium was approached from the initial states of dry pulp and pulp containing 66% of water. The phenol experiments were done in a thermostat between 45 and 50°C, and the filtration was also done at that temperature. In all cases the mixing of pulp and solution was adequate, and steeping took place for 18 hrs. before filtration took place. The results will be discussed very briefly, and the working data given for a few of the experiments only.

(a) Sodium Chloride Solution.

(i) Unbeaten Pulp.

Initial conditions (Wet pulp 8.555gms cellulose,
16.445gms water.
Solution 11.935gms salt,
45.724gms water
Total water 62.169gms

Final conditions. By calculation from the salt concentration of filtrate it is found that 11.935 gms salt are associated with 62.210gms water.

(ii) Beaten Pulp.

Initial conditions (Wet pulp 7.823gms cellulose,
23.684gms water.
Solution 11.946gms salt,
45.762gms water.
Total water 69.446gms.

Final conditions. As above by calculation, Total water 69.740gms.

The duplicate experiments gave similar results. The differences in the initial and final water contents are well within the limits of experimental error and show that no preferential adsorption of the solvent occurs.

(b) Sucrose solutions.

Duplicate experiments were done on the unbeaten pulp alone. The determination of the sucrose by evaporation of its syrup in vacuo was somewhat troublesome. It was not possible to use a cryoscopic method as a suitable thermometer was not available. The results obtained were however essentially similar to those obtained with common salt. In one case the final water was very slightly greater and in another case less than the initial water. There was no evidence of preferential adsorption of water.

(c) Phenol experiments.

These were a little troublesome, as adequate mixing had to be achieved of a concentrated pulp and a phenol solution at 45 to 50°C. It was inevitable that slight losses of solution took place. The phenol determinations in the filtrate were by the iodometric method of Messinger and Dortmann (See Cain and Thorpe, Synthetic Dyestuffs p. 312), and were concordant.

(i) Unbeaten Pulp.

Initial conditions (Wet pulp 8.850gms cellulose,
(17.086 - water.
(Solution 5.462 - phenol,
(44.150 - water
(Total water 61.236gms.

Final conditions. The filtrate contained 8.106% phenol. This by calculation gives final water content 61.92gms.

The difference can only be interpreted as a small preferential adsorption of phenol to the extent of 0.69% on the dry fibre. Another two experiments gave 0.3% and 1.9% respectively. By using dry pulp initially a still higher figure for adsorption was obtained.

(ii) Beaten Pulp.

Two experiments were done with wet pulp (25% cellulose, 75% water), and one with pulp which had been dehydrated with alcohol and allowed to air-dry afterwards. This had a residual moisture content of nearly 10%. In every case there was preferential adsorption of phenol by the pulp from the solution, the respective percentages for the three experiments in the order named being 2.23, 2.29 and 2.90 on the dry fibre.

It can safely be concluded therefore that there is no evidence that the solvent water is preferentially adsorbed by the cellulose in any of the cases which have been examined. The results are concordant, and the disturbing effect of adsorption has been minimised by using fairly strong solutions. Beaten and unbeaten pulps have shown identical behaviour under these conditions.

9. Density Measurements on Beaten and Unbeaten Fibre.

It has been pointed out during the discussion on the hydration of elastic gels that the total volume contraction of the system, gel + liquid, is probably the best measure of hydration. In the case of such a porous aggregate as a cake of cellulose fibres the true density is very difficult to measure with any

degree of accuracy. If the fibre hydrates like a typical elastic gel two things might be expected. (a) The density measured pyknometrically by immersion in a hydrating liquid should be greater than that measured in an indifferent or dehydrating liquid. (b) The density measurement of well beaten pulp in water should exceed that of unbeaten pulp.

In the course of the preceding work several measurements have been made during the determination of the C_h number. In all cases the use of mercury as a pyknometer liquid in contact with the wet pressed cake left something to be desired. The unbeaten cakes contained air which was not completely expelled, and the results are not worth recording. The well beaten cakes gave the highest figures, but in such cases it was necessary to correct the values for the rather high ash content of the beaten pulp. Some typical results using the mercury pyknometer are given on a pulp M6 beaten 70 hrs. in the pebble-mill (60gms pulp, 1000gms pebbles and 1500cc water) to beating degree 94.3°S.R. This pulp gave a C_h value 1790 (oven dried) and 2310 (slow dried). Three cakes were pressed in a normal manner for wet density measurements. The ash content of the pulp was 5.65% and the ash specific gravity was assumed to be about 2.5, as it was presumably all derived by abrasion from the stoneware jar. The results of measurements were as follows:-

	Wet weight	Dry fibre weight	Wet volume	Cellulose density
No. 352	21.139	8.175	18.012	1.586
- 353	20.931	8.058	17.937	1.558
- 354	21.076	8.007	18.043	1.573

The last column has been corrected for ash weight and density. The mean result is 1.573 ± .010.

Two further tests were made on another pulp in which the pressing was continued at 200 lbs. per sq. inch to an equilibrium, in the first case at 19°C, in the second case at 35°C. Thus more air was lost in the second case. The results were:-

	Wet wt.	Dry wt.	Wet vol.	Cellulose density
No. 346 19°C	17.731	8.117	14.725	1.554
- 348 35°C	17.051	8.015	13.904	1.610

It was recognised that pyknometer measurements should be made in either water or alcohol, and that the pulp should be properly exhausted in vacuo before filling the pyknometer with liquid. Several experiments were tried on these lines using the same glass pyknometer as was used for cohesion tests. It was easy to attach a capillary T tube to the neck of this, so as to be able to evacuate the pyknometer completely and fill it with the desired liquid without admitting air. The pulp was made into the form of a thin wet sheet and coiled inside the pyknometer, but in that case it was only possible to use the equivalent of 2 - 2.5gms. of dry fibre, and there was of course a volume error in closing the ground-in stopper of the pyknometer, which error became serious when such a small weight of pulp was used.

The experiments were therefore repeated with 8gm cakes of a highly beaten pulp, M11, beaten similarly to M6 for 50hrs. in the pebble-mill with a final beating degree of 93°S.R., and an ash content of 2.49%. The

cakes were pressed practically to equilibrium in the press, and at 2001bs per sq. inch as usual. The mean figure obtained for the cellulose density (ash corrected) was 1.573. On this occasion the results were fairly concordant. It was very difficult to obtain a good coherent cake of the unbeaten pulp, but using a cake of 5gms weight the density came to between 1.57 and 1.58. It did not therefore seem to be possible to distinguish between unbeaten and beaten cellulose by this method. It was recognised that the chances of error were somewhat greater when using mercury in the pyknometer, and also that it was a difficult matter to ensure the elimination of air. It was not possible with the time and opportunity available to go into the question of the density of beaten and unbeaten cellulose measured in water-free alcohol and other liquids. In the case of the few experiments done with industrial alcohol pressed cakes the densities came out too low in the mercury filled pyknometer, and somewhat too high if the pyknometer was filled with industrial alcohol. The latter experiments would point to the retention by the pulp of a layer of adsorbed water even after careful washing with 90% alcohol.

An excellent review of the existing state of knowledge on the question of the affinity of cellulose for water, alcohol and other liquids is given in a recent paper by R.O Herzog[139]. He quotes the pyknometric density of the natural fibres as ranging from 1.58 to 1.61, and of mercerised fibres at 1.52. The true density of the cellulose substance calculated from Xray measurements

comes out at 1.62. Herzog admits that there is adsorption of alcohol vapour by cellulose, but does not appear to find a resemblance between the behaviour of cellulose fibres in liquid alcohol and water respectively. Experiments have been done by W. Hellat[140] with exceptionally well dried fibres in salt solutions in 99% alcohol. He concludes that the residual water is all-important in the resultant adsorption phenomena.

10. SUMMARY.

(a) It is concluded that the most important effect of beating, apart from the mechanical reduction of fibre dimensions, is the development of a fibre surface property which promotes fibre-fibre bonding in the final sheet of paper.

(b) A method has been designed to measure this property, by determining the volume contraction of a standard pressed cake during a regulated drying process. The characteristic constant so obtained has been called the cohesion number of the pulp. There is a simple relation between this number and the final apparent density of the dried cake.

(c) Data are given for the purity of the cellulose used throughout the experimental investigation.

(d) Comparative value of cohesion numbers, flow-constants and Schopper-Riegler numbers are given, usually both in water and alcohol.

(e) The effect of beating in alcohol, petrol and water has been discussed, also the cohesion numbers of asbestos cakes. The effect of dehydrating the pulp progressively in alcohol-water mixtures has been discussed.

(f) It has been shown that in the case of standard pressed cakes the volume-weight drying curve is linear over a considerable range for different degrees of beating, and that it is probable that a small percentage of water is adsorbed by all pulps without volume change.

(g) It has not been definitely shown that the steeping of beaten pulps in salt solutions changes the cohesion number in accordance with the lyotrope series effect on other elastic gels, nor that steeping in buffered solutions of varying pH value, nor in dilute acid or alkali up to $\frac{N}{10}$ concentration has any effect on this. Boiling the pulp in water is also shown to be without effect.

(h) It has been shown to be quite impracticable to determine the imbibition water in beaten pulp by measuring the water retained after pressing to equilibrium at a pressure of 200 lbs. per sq. inch.

(i) It has not been found possible to determine the 'bound' water in beaten or unbeaten pulp by a negative adsorption method.

(j) It has not been found practicable to measure the presumed condensed surface layer of adsorbed water on beaten pulp by a density method. The density of the beaten pulp used has been found to be about 1.573.

References.

IX.

139. R.O. Herzog, Wochenblatt Pap.Fab.61.541.(1930)

140. W. Hellat, Koll.Z.50.265.(1930)

141. Other references to cellulose density determinations ---

A.T. King, J. Text. Inst. 17.53T.(1926) density

of wool in various liquids - high densities as in water, $CH_3(OH)$ where adsorption occurs - low densities in C_6H_6 etc. where no adsorption.

Another article Wochenblatt Pap. Fab. 24A.36.(1925) adopts 1.579 as the pyknometer density of sulphite cellulose in water.

Yoshida and Takai. J.Cell.Inst.Tok. 7(255)(1931) find the density of purified ramie fibre to be 1.614.

See also Williams on charcoal ref. 144.

X

PROPERTIES OF SHEETS MADE UNDER VARYING CONDITIONS.

The development of the desirable properties of sheet strength and uniformity of texture by the beating process is a vast subject which has been dealt with by many writers. Only those parts of this subject will be briefly discussed which have a direct bearing on the work which has been already described. The progress of dehydration by alcohol will be studied in the properties of sheets made in mixtures of alcohol and water with a progressive rise in the alcohol fraction. The properties of sheets made from the pulps beaten comparatively in petrol, alcohol and water will be examined. Finally a series of results will be given on the progressive change in sheet properties as pulps are beaten in water: (a) on the industrial scale, (b) in a model laboratory beater where the cutting effect predominates, (c) in the pebble mill where the mechanical treatment is comparatively gentle. Figures will also be quoted to show the change in fibre dimensions during the treatment. Thus the 'beating degree' Schopper-Riegler number and the Cohesion number will be given alongside the mechanical properties of the sheet of paper produced. The data must be regarded as by no means exhaustive, but only as an illustration of the preceding investigations, and as showing that the essential phenomenon of beating, the development of the colloidal surface film, is always present whatever may be the mechanical conditions of

the operation. The experimental work on sheet properties has for the most part been done contemporaneously with that on the cohesion property, and on the same beaten pulps.

1. Experimental Methods.

A comparatively simple method had to be adopted for sheets made in alcohol or alcohol-water mixtures, in order to economise liquid. In this case the sheets were always made of a substance about 40 lbs per Demy ream of 480 sheets. This trade measurement was used, as it was convenient for comparison with industrial paper data, and because it was very easy to weigh the sheets rapidly on a lever balance reading directly in terms of this unit. For comparison it may be pointed out that 26.88 lbs. Demy = 100 gms. per sq. metre. The strength tests used were the burst test with an Ashcroft tester reading in lbs per sq. inch and the tear test with an Elmendorf tester. The air porosity of the sheets is also thoroughly empirical, as the volume of air was measured which was sucked through a paper circle of one inch diameter under an initial negative head of water of 2 feet which diminished uniformly to zero after 50 cc. of air had been sucked through. The standard time for this test is 15 secs., but for comparative purposes the time has had to be reduced to 5 and even 2 secs. in some cases where the air porosity was excessive. The thickness of the sheets was recorded in units of mils or thousandth parts of an inch. As all the testsare comparative, there is

little disadvantage in such unrelated units of measurement. Only one correction has been applied. The burst and tear tests have occasionally been expressed as a multiple of the Demy weight.

In such cases the sheets have been made by suction on an ordinary Buchner funnel. The volume of liquid used is 350 cc. The size of the funnel is just such as to accommodate an 11 cm. filter paper, but the base of the funnel has usually been covered with a disc of linen cloth in preference to the paper. The sheets are easily removed from the linen disc and are transferred in fours to a square of cotton cloth and pressed in a couching press at a final pressure of 200 lbs per sq. inch for 2 minutes between a steel plate and 6 sheets of dry blotting paper. The drying has been done in 10 minutes on the surface of a copper cylinder electrically heated to 100°C surface temperature. This cylinder was surrounded by a thick felt jacket pressed lightly upon the cylinder surface. Before testing, the sheets have been conditioned for 24 hours in a conditioning box over a dish of sulphuric acid of the correct density to maintain the atmosphere at 70% relative humidity.

In those cases where the progress of beating has been studied in water it was possible to improve the procedure. The pulp in such cases was always disintegrated for 10 minutes at not over 1% concentration in a disintegrating churn in which a propeller revolved at 1000 revolutions per minute. The 8 inch

square sheets were made on the Wilén machine on a wire-cloth of 90 meshes per inch and from a volume of about 1500 cc. suspension. Couching was on to a stainless steel plate and was helped by rolling a heavy brass roller over the plate when lying in contact with the wire. Beyond this the method is essentially the same as that described above. A fuller account of the technique is given in the already quoted paper by MacDonald and Cramond (133), except that it must be noted that the couching pressure is given in three stages, as the sheet from the Wilén machine is necessarily wetter than one which has been compacted by suction on a Buchner funnel. The above paper also gives an excellent idea of the reproducibility of results.

2. Dehydration by Alcohol.

The effect of the dehydration by alcohol of well beaten pulp is very obvious in the sheet properties from either unbeaten or well beaten pulps. The effect of conditioning the sheets is also different for alcohol and water made sheets. The following table illustrates these effects.

Made in	Condition	No. sheets	Wt. Dy.	Bulk Mils	Porosity 15 secs. air cc.	1 sheet Tear	Burst
water	dry	4	43	10	2.6	43	112
"	70% R.H.	4	44.2	11	3.1	57	119
alcohol	dry	4	43	13	38.6	44	34
"	70% R.H.	4	44.4	13.2	34.5	44	37

The texture of alcohol and water made sheets is obviously very different. Comparative tests on the rate of picking up water vapour from a 90% saturated atmosphere, in a box where active air circulation was provided by a fan showed this difference very well. The following table shows the amount of water adsorbed during different times of exposure by the alcohol and water made sheets respectively.

Minutes exposure	5	10	30	960
(water made) moisture%	1.18	1.76	3.10	7.63
(alcohol made) " "	6.05	6.98	7.04	7.68

In each case the final condition was the same. The above sheets were made in January 1928 from a well beaten, long fibred pulp. Other tests with a very short fibred pulp showed much lower comparative tear figures for alcohol made sheets. The alcohol used is the industrial methylated alcohol, previously described.

Analogous results are also available using unbeaten pulp which has been broken up by a 20 minutes treatment in the disintegrating churn. In this case the porosity test has been taken for 1 second only as the sheets are of open texture. Eight sheets are made in each case and the average percentage deviation from the mean is given after each measurement.

	Water made	Devn.%	Alcohol made.	Devn.%
Weight lbs. Dy.	45.4	1.8	44.0	7.7
Bulk mils.	10.0	4.4	15.0	8.3
Porosity cc.	14.2	16.6	34.6	5.8
Single sheet tear	51.6	8.5	12.2	27.8
Burst 4 tests per sheet	41.1	5.8	8.1	15.4

The above figures will show how difficult it is to obtain reproducible results on alcohol made sheets of unbeaten pulp. Of course the burst figures are too small to be reliable. In the case of a well beaten pulp the accuracy is much greater.

The change in sheet properties as sheets are made of the same beaten pulp in alcohol-water mixtures will be illustrated from a lightly beaten pulp Db. Unfortunately in this case the sheets for the middle point of the series at 50% alcohol were accidentally destroyed and could not be replaced.

This pulp was beaten as follows - 60 gms. dry fibre, 1500 cc. water, 2000 gms. pebbles for 3½ hours. Two lots were made and mixed. The final beating degree was 41° S.R. and the C_h number was 564 in water and 174 in 90% alcohol. A summary of the sheet tests is given.

The results of the first and second group of tests are illustrated graphically as far as relative burst and tear ratios are concerned on page 158A. Thus comparative dehydration effect on flow-constants, cohesion numbers and sheet properties can be seen together.

% Alc.	Dy. wt.	No. sheets	Bulk mils	Air Porosity cc.	Single tear	Burst	T / Dy.	B / Dy.	Relative T / Dy.	Relative B / Dy.
nil	44.6	12	9.0	3.0	61.3	94.0	1.375	2.108	100	100
20	48.2	6	10.2	7.1	79.5	89.1	1.649	1.849	120	88
30	47.0	12	10.2	14.2	77	80.3	1.638	1.708	119	81
71	46.5	4	12.0	17.9	54.5	44.8	1.172	.963	85	46
90	46.7	6	11.8	31.7	30.5	23.0	.653	.492	47	23
96	47.0	6	13.6	31 (2.)	27	18.2	.574	.387	42	18

Note The air porosity measurements are taken over 5 secs. except the last two where 2 secs. only has been allowed.

One other set of results will be given below, in order to show how difficult it is to get reproducibility, and how it would not be fair to draw the inference that the variation in sheet properties is a sudden one somewhere between 30% and 70% of alcohol. In this case the results for 70, 50, 30 and 20% alcohol mixtures are to be inserted between the data in the table of page 192 for 90% alcohol and water sheets. The completed figures are as follows:-

% Alc.	Dy. wt.	Bulk mils	5 secs. Air porosity cc.	Single Tear	Burst	T / Dy.	B / Dy.	Relative T / Dy.	Relative B / Dy.
0	44.2	11	3.1	57	119	1.290	2.692	100	100
20	41.6	10	3.7	38	89	.913	2.140	71	80
30	43.4	10	10.7	42	86	.968	1.982	75	74
50	44.3	10.8	8.9	57	86	1.287	1.941	100	72
70	41.7	10.7	22.3	49	55	1.175	1.319	91	49
90	44.4	13.2	34.5	44	37	.991	.833	77	31

It is often difficult to make satisfactory sheets with 30 - 50% alcohol-water mixtures on account of the high viscosity of the liquid, which makes it more difficult to obtain uniform distribution of the fibres in the sheet. The change in the ratio of bursting strength to substance is the most significant feature of the dehydrating action of alcohol. The effect of dehydration on the tear ratio is irregular. It is in fact the case that the progressive hydration of a well beaten pulp starting from the 90% alcohol end of the series shows the same sequence of sheet properties as would be exhibited from normal sheets of the same pulp at successive intervals of the beating process. The change in bulk and air porosity runs along similar lines. It has been shown during the course of these experiments that the dehydrating action of alcohol is reversible within limits of experimental error for the sheet properties, just as it is for flow constant and cohesion number.

Before leaving this question it may be mentioned that sheets were made in the appropriate liquid and also in water for the experiments where pulp was beaten comparatively in water, alcohol 90% and petrol. The results are given below, and if the burst test results are compared with the cohesion numbers (see IX, page 161) it will be agreed that the cohesion number can be used to predict sheet properties to a certain extent, although of course it does not allow for fibre length changes. The sheets made in water have been

made on the 8 inch square Wilén machine, the alcohol and petrol sheets on the small Buchner funnel.

Sheet of pulp	Sheet in liquid	Dy. wt.	Bulk mils	Air porosity cc.	Air porosity secs.	2 sheet tear	Burst	2T / Dy.	B / Dy.
Gb	petrol	50.5	13	40	5	32	6	.633	.119
"	water wetted	53.5	11	33	5	58	26	1.084	.486
Gc	alcohol	51	12	33	5	40	19	.784	.373
"	water wetted	45	8.5	8	5	80	67	1.778	1.618
Ga	water	45.8	6.0	3.2	15	74	107	1.616	2.336
"	"	45.2	6.5	3.5	"	70	99	1.549	2.190
Gb	water	42.5	6.5	17.3	"	67	64	1.713	1.506
"	"	39.4	6.0	29.4	"	58	55	1.472	1.396
Gc	"	43.9	7.0	15	"	93	78	2.119	1.776
"	"	43.1	6.5	7	"	72	78	1.670	1.810

Ga beaten in water, Gb in petrol, Gc in industrial alcohol.

Notes on above table.

(a) The second and fourth lines denote tests on sheets which have been made in petrol and industrial alcohol respectively, dried, wetted with water and dried again.

(b) The Tear tests in this table are the tests on 2 sheets torn together, hence the figures are larger than in previous tables.

(c) The results show how it is not easy to rewet and press a sheet after making, so as to get the same results as if the sheet had been made in water.

A number of sheets were also made from beaten asbestos pulp. As was to be expected there was no surface cohesion. The average tests on a 30.7 lbs Dy. sheet were as follows:

Bulk 10 mils, Tear on 6 sheets 39, Burst too small to be measurable.

3. The function of felting during drainage, and of wet pressing during sheet making.

In order to discover to what extent the mechanical qualities of the sheet are due to the felting of the fibres during drainage on the machine wire, and to what extent the pressing of the wet sheet is responsible, a number of experiments were done on a well-beaten stuff Fb of beating degree 95° S.R. It was thought that some additional light might be shed on the sheet making process by introducing the hydrating and dehydrating action of water and alcohol respectively at different stages of sheet formation. It is recognised that the general problem of the effects of felting on the wire and wet pressing have been far more comprehensively dealt with by other investigators, both on the laboratory and industrial plane. Briefly the experiments were as follows: (a) to form the sheet in water and to dehydrate just after formation, or just after pressing, (b) to form the sheet in industrial alcohol and to rehydrate with water at the above stages. Experiments were also made using light petrol, but it was found to be difficult to replace this by water, and impossible to

perform the reverse process in a satisfactory manner. Among the water-made sheets are included two sets of sheets, (1) made from the same pulp after heating to 70°C for an hour and forming the sheet at this temperature, (2) from pulp boiled one hour in $\frac{m}{1300}$ $Al_2(SO_4)_3$ solution and cooled before making into sheets. A brief summary of results is given below.

	Sheet	Dy.wt.	Bulk mils	15 secs. Air Porosity cc.	Tear 1 sheet	Burst	$\frac{T}{Dy.}$	$\frac{B}{Dy.}$
1	water	44.0	7.5	1.9	37	123	.841	2.795
2	hot water	41.0	7.0	1.8	38	111	.927	2.707
3	after boiling	43.0	7.6	2.0	34	103	.790	2.395
4	dehydrated on Buchner	42.0	7.5	2.1	29	73	.690	1.738
5	petrol	41.1	11	10.3	22	15	.535	.365
6	alcohol	44.0	9.5	6.2	42	44	.955	1.000
7	water wetted Buchner	43.3	7.2	2.0	37	98	.854	2.263
8	wet after pressing	43.0	7.0	1.9	36	98	.837	2.279

The suction on the Buchner gives a certain degree of wet pressing.

Notes on the above table.

(a) In each case 4 - 6 sheets have been made. The deviations between the tests are very similar in amount to the percentages quoted in the first table (p194) illustrating the difference of water and alcohol made sheets. It has been necessary to repeat

quite a number of experiments where the discrepancies were greater.

(b) In the case of test 4 the already formed sheet has been washed with industrial alcohol on the Buchner funnel before pressing. A similar procedure but with water in place of the alcohol has been adopted for test 7. In the case of test 8 the sheet has been thoroughly water wetted after pressing, and again pressed before drying.

(c) Test 5 has been made from the same pulp, by displacing the water successively with alcohol, acetone and petrol before sheet making.

It is clear from the above tests that fibre felting during drainage on the paper machine wire can be expected to take place just as well in an alcoholic medium as in water, and that strength properties can be imparted to the dehydrated sheet at any stage before drying, provided that the sheet is finally pressed adequately when water wetted. This latter point is not illustrated in the table, but has also been experimentally established, for an alcohol made and pressed sheet will still maintain a certain looseness of texture even after being wetted with water. A similar series of tests has also been made with a slightly beaten pulp, but the results being entirely similar to the above have not been quoted. It need only be pointed out that occasionally the tear tests behave abnormally with too well beaten pulps, and it is possible in some cases to record a higher tear with

an alcohol-made sheet than with a water-made sheet. On inspection the latter sheet can be shown to tear across the individual fibres themselves, giving a short length of tear, whereas the alcohol-made sheet gives a long tear with greater consumption of energy, the fibres being torn apart without being individually broken. Such a result occurs more usually with sheets which are too dry and have not been conditioned to 70% humidity.

4. Typical Test Data during the Progress of Beating.

Throughout the present thesis the view has gradually been put forward that the peculiar properties of beaten pulp, as compared with unbeaten, are mainly dependent on the formation of a hydrated surface film on the cellulose fibres. As a result most of the experimental work has been done on pulp which has been beaten to a far greater degree than ever occurs in the industrial processes of paper making. It has appeared desirable therefore to study the variation of pulp properties throughout typical beating processes so as to render possible a comparison between industrial scale and laboratory beating operations. Three typical cases will be considered. In each case the Schopper-Riegler beating degree and the cohesion number will be followed, alongside the properties of sheets made from the pulp at various stages of beating. In two of these cases microscopic measurements will be given, in order to show the change in fibre dimensions during beating. All the sheets have been made on the

model Wilén machine, pressed, dried and conditioned according to the method already described. In most cases tests have been made on the Schopper tensile breaking tester as well as for burst and tear, but the results are not recorded except in one case, where the individual tests of a batch of sheets are all given, in order to show the degree of variation between different sheets made from the same batch of pulp. In all cases the specific weight of sheet aimed at is 26.88 lbs per Dy. ream of 480 sheets or 100 gms / sq. M. This practice was in accord with the laboratory routine where wood pulps were being tested for comparative strength, with a view to comparison with results on the industrial scale. The columns 'tear ratio' and 'burst ratio' are the ratios of the tear for 6 sheet thickness (tear numbers are additive) and the single sheet burst to the Dy. weight of the sheet.

First Series of Tests.

This series of tests was done on a typical beating operation on the industrial scale, on a mixed furnish of about equal proportions of esparto and sulphite wood pulp, in order to produce a fairly strong white paper for drawing purposes. The pulp concentration in the beater was 5 - 5.5%. The finished paper gave a tear ratio of 4.724 across the sheet, and a burst ratio of 1.620 and was about 27 lbs Dy. wt. The test figures are given below.

Hours beaten	Beating degree °S.R.	Cohesion number	Tear ratio	Burst ratio	Air porosity cc.	
1.25	19.9	205.1	5.048	1.368	5 secs.	50 cc.
2.17	24.0	242.8	4.702	1.433	5 "	47.2 cc.
3.67	29.6	250.9	6.428	1.897	10 "	49 cc.
5.17	27.2	284.6	5.607	1.876	15 "	43 cc.
6.67	46.7	301.6	5.674	1.864	15 "	28.5 cc.
9.0	53.7	318.2	5.293	2.011	15 "	24 cc.

In each case 3 sheets were made from a batch of pulp. On each sheet the burst was determined as the average of 5 tests, and the tear on 2 pieces torn together. The tear and burst ratios were determined separately for each sheet and the results averaged.

Second Series of Tests.

A beating test was conducted on the same bleached sulphite wood pulp which has been used throughout the experimental work. The model beater in the laboratory was furnished with 40 litres of water. The pulp concentration was 2¾% dry fibre. The knives of the roll were fairly sharp and of phosphor-bronze. The object of the experiment was to beat under fairly severe conditions where the tendency would be to cut the fibres rather than to draw them out gently. Reasonably large samples of pulp could be withdrawn at intervals without materially altering the concentration of the remainder. The roll of the beater was, however, too light to give the drastic action which was desired at the finish of the beating. The test

figures are given below.

Hours beaten	Beating degree °S.R.	Cohesion number	Tear ratio	Burst ratio	Air porosity cc./15 secs.
1	20.3	209	6.699	1.810	41.2
2	24.5	276	5.655	2.042	31.3
3.5	42.7	509	5.434	2.676	11.9
5	71.3	739	4.765	2.606	10.6
7	83.8	1077	4.360	2.207	13.1
9.7	88.0	1438	2.982	2.004	13.9
19.2	91.4	1634	2.948	2.153	9.7

Third Series of Tests.

Finally a series of tests was made with the pebble mill. The pulp concentration was 4% dry fibre. 1000 gms. pebbles were used in each jar with 1 litre of water. In this case it was necessary to beat a charge of pulp for each test, as it was not possible to withdraw some pulp at an intermediate stage and proceed with the beating in the same jar. Although the speed of the jar mill motor was reasonably constant it was found to be difficult to reproduce the beating effect with any degree of accuracy on repeating an experiment. The object in this case was to give a comparatively light mechanical action so that the colloidal surface film should be well developed without too much sacrifice of fibre length. In each case 4 sheets were made. In those cases where the beating degree number was very high (°S.R. $>$ 85) it was difficult to make the sheets on the Wilén machine

as drainage was very slow. It was also difficult to regulate the sheet weight as fine fibre débris escaped to some extent through the meshes of the wire. Considerable shrinkage of sheets developed during drying. The results of the pebble mill tests appear below.

No.	Hours beaten	Beating degree °S.R.	Cohesion number	Tear ratio	Burst ratio	Air porosity cc./15 secs.
M 7	1	22.3	715	6.254	1.907	29
M 8	3.5	36.3	901	5.827	2.249	15.5
M 10	5.5	60.3	1601	5.499	2.454	5.3
M 9	8	82.3	2063	4.555	2.545	4.1
M 6	70	94.3	2302	3.122	2.039	2.5

It is regrettable that in this case the cohesion numbers are not accurately comparable with the ones in the previous tables, as the cakes have been dried in a desiccator and not in the oven. The numbers are therefore somewhat higher, although they are all comparable with each other. Pulp M 6 for instance is known to have an oven dried C_h value of 1790.

As a matter of interest it may be remarked that the pulp used for these experiments if made into sheets without beating gives a tear ratio of 6.522 and a burst ratio of 1.388.

The group of individual measurements which follow are from sheets made from pulp M 7. They are quite typical of the results of other experiments as regards accuracy.

No.	Wt. lbs Dy.	Bulk mils	15 secs. Porosity air cc.	2 sheet tear	Tensile break	Tensile stretch	Burst.
71	26.5	4.9	28,32	52	16.1 17.4	2.8 3.5	51
72	26.5	5.0	30,31	62	16.5 17.5	3.2 3.6	50
73	27.5	4.7	26,27	54	19.0 19.0	3.5 3.6	54.5
74	26.5	4.5	26,32	55	15.0 18.7	3.0 3.5	48.5
Av.	26.75	4.8	29	56	17.4	3.3	51
Dev %	1.4	3.7	7.9	5.4	6.6	8.0	3.5

In the above table the tensile figures have been included. The ratio of tensile breaking strength to substance follows the burst ratio pretty generally. This is not always the case however, as the tensile strength develops a maximum at a different stage of the beating from the bursting strength maximum. The burst tests on each separate sheet may differ among themselves to the extent of over 10% deviation from the mean value.

In the case of the second and third series of beating tests samples of pulp were examined for fibre length and diameter by the microscopic method. Measurements were made on fibre slides with a micrometer eyepiece which had been standardised on a micrometer scale. It was unnecessary to use a high magnification. With a $^{2}/_{3}$ inch objective and the micrometer eyepiece 50 divisions on the focal scale of the latter were

found to measure .96 mm. The field occupied 2.2 mm. and was generally large enough for the longest fibres. The practice was to make 4 slides from each pulp sample and to measure from 50 - 100 fibres on each slide. In the case of diameter measurements it must be admitted that they afford no true guide as to the swelling during the beating process. As the beating progressed there was an increasing proportion of fibre débris which was not properly measurable. The mean results of the measurements are given below.

Second Beating Test, Laboratory Beater.

Hours beaten	2	5	7	9¾	12	15¾	19
No. of measurements	225	240	330	211	248	350	350
Av. fibre length μ	893	492	394	374	293	250	201
Av. fibre diameter μ	30	54	53	65	43	31	33
No. of measurements	150	136	201	129	240	350	350
Fibre Débris (estimated)				25%	50%	all fibrillated over 50% débris	

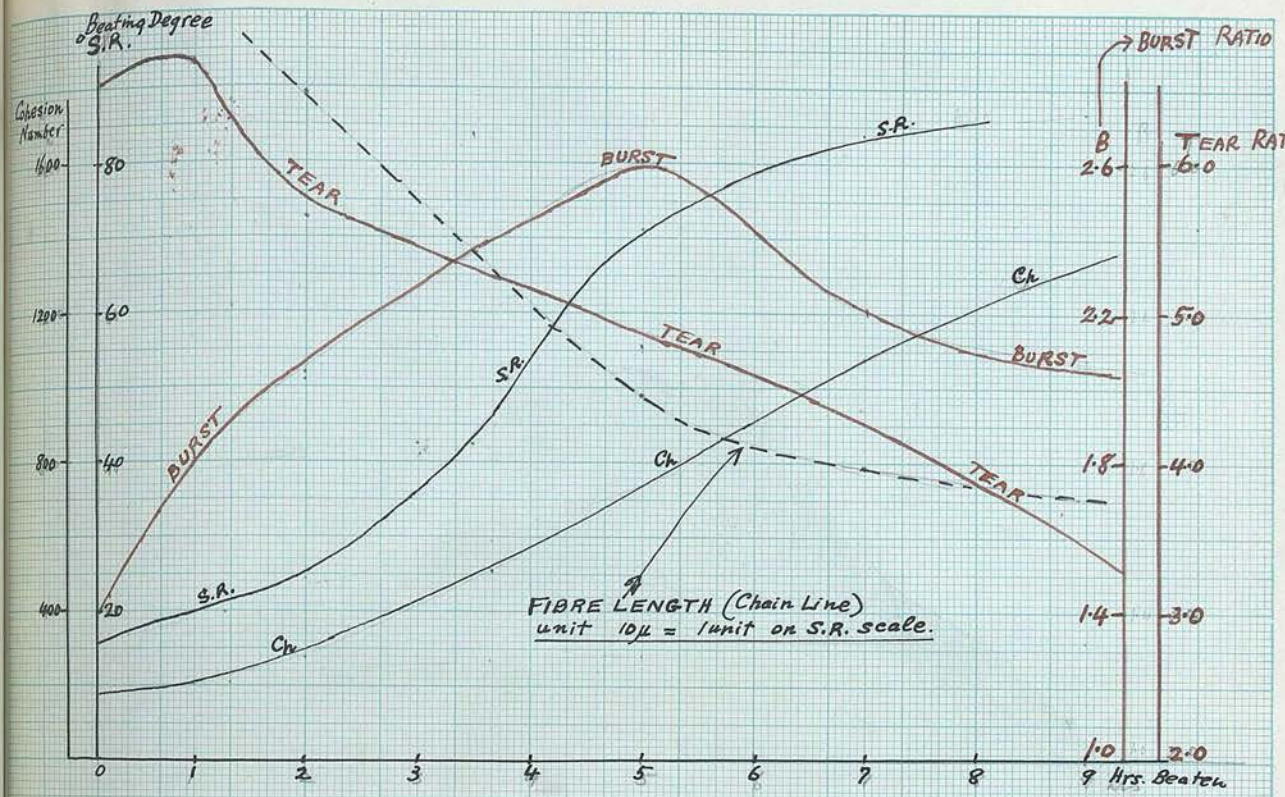
The fibre lengths and apparent diameters are measured in terms of μ = ·001 mm. The number of measurements made are given on the line above for lengths and the line below for diameters. The last line is a descriptive estimate of the amount of fibre débris on the slide. It will be noted that some of the samples do not correspond to the sheet test samples.

Third Beating Test, Pebble Mill.

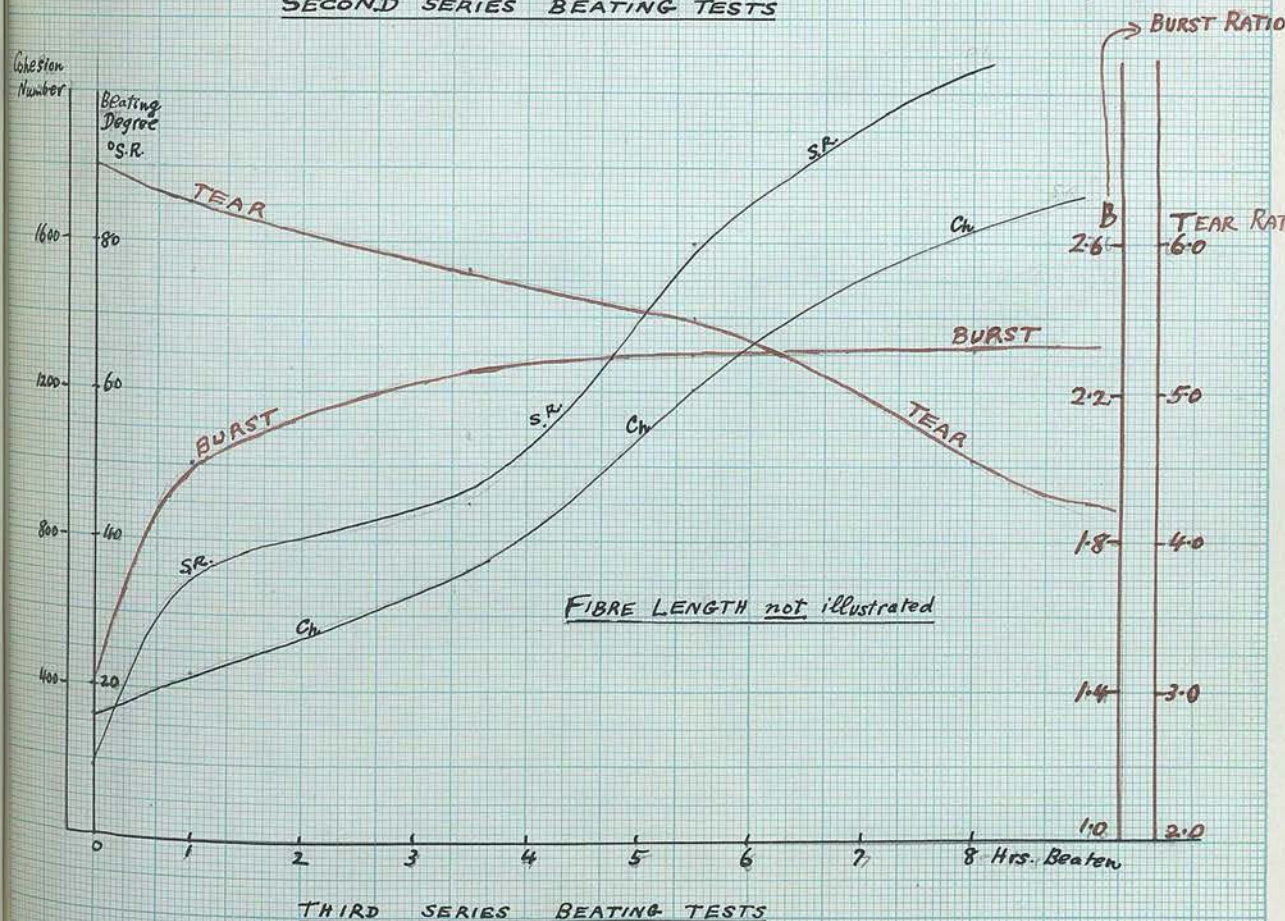
In these experiments the apparent fibre diameter only varied between 30μ and 35μ, and diameter measurements are not recorded. There was much more fibrillation. Consequently the slides were difficult to measure. Again an estimate is given of the percentage of fibre débris present.

Pulp	M 7	M 8	M 10	M 9	M 6
Hours beaten	1	3.5	5.5	8	70
No. of Measts.	140	208	191	155	80
Av. length (μ)	759	540	778	683	774
Description		much long fibre, curled and twisted	not much débris		very much twisted and fibrillated - no cutting

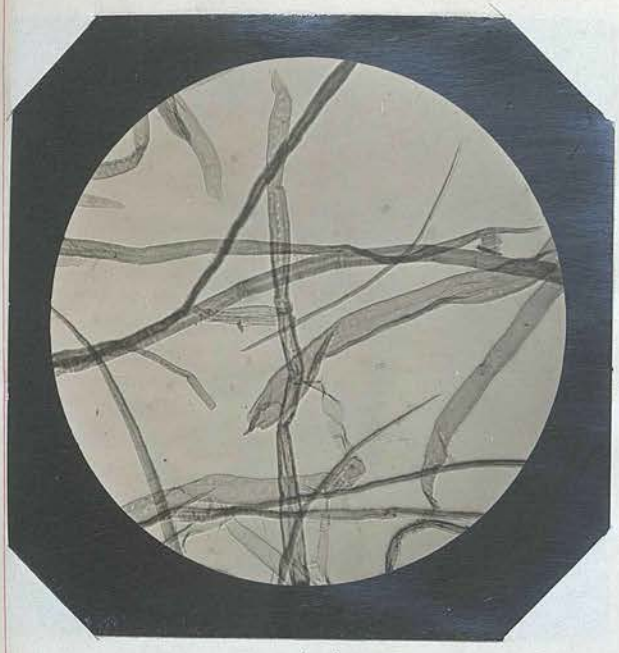
The abnormal figure for pulp M 8 calls for remark. M 7 and M 8 were beaten together on the pebble mill and it may have been that a slight increase of speed was responsible. It is also difficult to count the slides in the same way, as short fibres are sometimes measured as such and sometimes classed as débris. The general result is manifest however that fibrillation and formation of débris, with preservation of the length of the remaining fibres is the characteristic effect of light treatment in the pebble mill. Several microphotographs of beaten fibres are included on the next page, along with graphs of the beating tests.



SECOND SERIES BEATING TESTS



THIRD SERIES BEATING TESTS



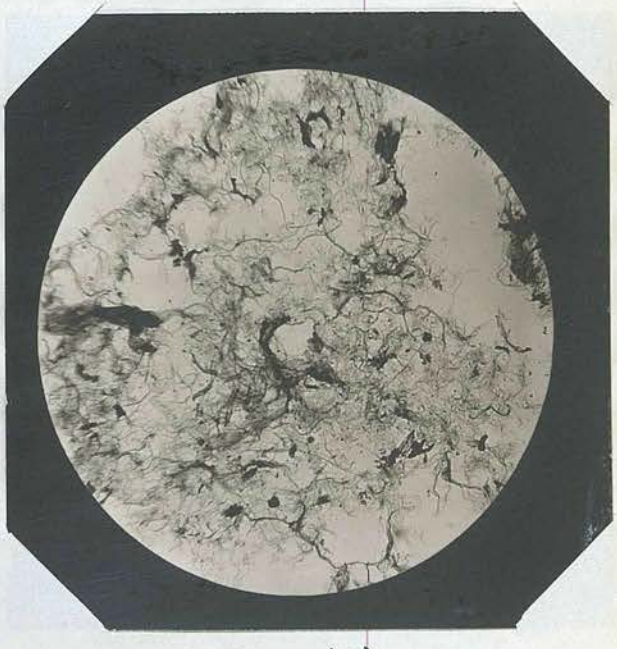
(1)
Unbeaten Pulp M
showing tracheids and pits.

(2)
Petrol beaten Pulp Gb
(p161) no fibrillation.

PULP MICROPHOTOGRAPHS

The author is indebted to Mr. Balsillie of the Royal Scottish Museum, Edinburgh, for these microphotographs of the beaten pulps used in the experimental work of this thesis.
The magnification is 70 diameters in all cases.

(3)
Well beaten Pulp M11 (p184)
Note extreme fibrillation
without cutting.



(4)
Lab. beater Test, 19hrs.
beaten (p207) mostly
debris.

5. Summary.

(a) A method has been described for the study of the mechanical properties of the sheet of paper produced from a beaten pulp, and has been applied to the study of the dehydrating action of industrial alcohol on stuff beaten in water. It has been shown how the sheet properties change progressively with the hydration of an already beaten pulp, in the same way as with the progress of the beating operation on an unbeaten pulp.

(b) The comparative effects of beating in water, petrol and alcohol have been studied, also the properties of asbestos sheets.

(c) It has been shown that no appreciable change in sheet properties results from prolonged steeping, and little by boiling in dilute solutions of electrolytes.

(d) It has been shown that felting of the fibres can take place perfectly well in a nonaqueous liquid, and that the formation of a colloidal surface film by water must be the main factor in the sheet bursting strength. This action would appear to be extremely rapid.

(e) In several typical beating processes beating degree and cohesion test data have been recorded along with sheet properties and fibre measurements. The cohesion number is shown to give an indication of ultimate sheet bursting strength, until the strength

falls off owing to excessive shortening of the fibre.

Reference.

142. W. Lüdtke Koll. Z. 341. (1929) gives an excellent paper on the mechanical strength properties of artificial silk threads and of cellophane when immersed in different liquids. The water content of the liquids appears to be of the greatest importance. Salt solutions were investigated. A lessened stretch accompanied greater strength and vice versa. The author groups liquids into hydrating, inert and dehydrating, and the classification goes parallel to the order of surface tension of the liquids.

XI

SUMMARY AND CONCLUSION.

1. The general relationships of fibrous cellulose and water, particularly as they apply to the papermaker's beating process, have been fully discussed in the theoretical half of this thesis. The experimental half has been chiefly devoted to the working out of some of the practical results to be expected from the hypothesis that the main feature of the beating process is the formation, on some part of the fibrous surface at least, of a colloidal or hydrated surface film which functions in some way during the drying process so as to promote fibre-fibre bonding and the development of strength in the resultant sheet of paper. It is true that fibre cohesion is the only phenomenon which is actually observed at first hand, and that the evidence of hydration is largely circumstantial, yet the study of the dehydration phenomena produced by ethyl alcohol, and to a lesser extent the cohesion behaviour of non-cellulose cakes, seem to show that water plays a unique and essential part in the whole range of phenomena. It is unnecessary at this point to do more than state and critically examine the main conclusions, as the discussion has been fairly complete in the theoretical half, while each experimental part concludes with a summary of the matter discussed. The guiding principle of the present criticism will be that no line of experimental approach to the central phenomena of beating is justified unless it falls reasonably into line with the fibre cohesion phenomena which are the desired outcome of the beating process. As this does not appear to be

the case with a good part of the drainage and electrokinetic phenomena, as well as vapour pressure and negative adsorption determinations, it is considered desirable to state the main conclusions first and endeavour to account for the discordant results afterwards.

2. General Behaviour of Cellulose.

Evidence from both physical and chemical sources agrees in showing that cellulose in all its forms is prone to exhibit hydration phenomena. The artificial silk industries are founded on this characteristic of cellulose. This behaviour of cellulose is generally explained on the basis of a loose micellar structure with the potentiality of liberating free residual valencies under certain conditions of strain. Sponsler has interpreted this characteristic of cellulose in a recent paper(23A). Perhaps one of the most interesting recent accounts is by F.T. Peirce(143) who states that water does not penetrate within the crystallites, that it leaves the longitudinal cohesion of the fibres unimpaired and only affects the transverse fibre cohesion, which latter is due to hydroxyl groups. He allows one active (OH) group to each ($C_6H_{10}O_5$) unit, and points out that this group can hold one (H_2O) group firmly in an orientated manner, so that other (H_2O) groups may also be held a good deal more loosely. Thus a water-wetted cellulose would consist of aggregates such as -

Cell. - OH - HOH . . . . . HOH - HO - Cell.

and in the course of drying, successive water molecules would be eliminated, until at last the two cellulose units would cohere firmly by their (OH) groups. The

picture is incomplete without bearing in mind that some of the hydroxyl groups of cellulose are of basic and some of acidic function. It is clear that this latter fact is all-important for the solvent action of the viscose, cuprammonium and zinc chloride reagents on cellulose. It is probably equally so for the range of phenomena with concentrated salt solutions dealt with by Von Weimarn. It is clear that the phenomena of beating hydration are altogether different, and that they need not imply any such strain on the cellulose micelle. In particular it is probable that no degradation process, even a partial one, is an essential part of the beating phenomenon. Even the Von Weimarn salt solution swelling phenomena do not imply any change in size or structure of the micelle as far as Xrays reveal the structure, and it is therefore unlikely that the beating process will show any alteration in micellar structure as revealed by Xrays, viscosity of cuprammonium solution, or copper number.

3. Direct Evidence of Water Bonding in Beaten Cellulose.

It must be frankly admitted that such evidence is meagre, and at the best indirect.

The rate of evaporation method as carried out by Rowe(108) is somewhat difficult to assess, since Fisher by its means would have found evidence of the existence of similar amounts of 'bound' water in such materials as wet sand and, apart from other considerations, such 'bound' water was not found by the freezing out method of Rubner and Thoenes. Also Rowe found that steeping

of beaten cellulose in water diminished hydration, whereas there is no evidence that the cohesion properties of the fibre diminish in this way. Nor is there any evidence that beating modifies the vapour pressure isotherm of water-wetted cellulose to any extent at all. Recent researches(104-105A) are fairly conclusive on this point. The modern methods for the assessment of 'free' and 'bound' water have not yet been exhaustively applied to the beating problem, but such experimental work as has been done, including that described in the present thesis, has shown negative results. There are as yet no comprehensive and really satisfactory measurements available to show that there is no total volume contraction of the system when cellulose is immersed in water, or to show that cellulose does not have a higher density in water than it has in dry ethyl alcohol, or in a dry hydrocarbon liquid. The difficulties incidental to such experimental work are considerable. The present author has endeavoured to show that the apparent density in water is the same for beaten pulp as for unbeaten fibres, and any large discrepancy would certainly have been detected. What is wanted in this connection is careful experimental work like that of Williams(144) on charcoal, by which the latter inferred the presence of a condensed water layer on the charcoal surface under a pressure of about 40,000 atmospheres. The pressure-imbibition water determination as recommended by Strachan and carried out by the author and others is unsatisfactory as a practical test, and cannot be held to distinguish between

water held in the fine capillaries by surface tension forces and water of imbibition held according to the ideas of Katz. This is the more unfortunate in the case of a phenomenon like beating where there must be a continuous decrease of capillary size and an increase of specific surface. It would indeed be desirable if the actual increase of specific surface during beating could be approximately measured. Microscopic methods must fail with fibrous bodies which can be fibrillated like cellulose, and of which the micellar structure is known to be loose. The adsorption method is open to many objections but has not been thoroughly investigated. The interpretation of vapour pressure and 'bound' water results in terms of an adsorption or imbibition film is obviously dependent on our knowledge of specific surface. Nelson and Hulett(145) have pointed out that a unimolecular water layer on a surface of 600 square metres would amount to 0.186cc. A previously quoted figure (p. 47) gave 1000 sq. metres as the approximate surface of one gm. cellulose split up into its constituent micelles. The unimolecular water layer would therefore correspond to a water content of 31% by weight, all of which water would be completely orientated and without vapour pressure. In actual beating it was pointed out that the specific external surface was unlikely to exceed 0.5 sq. metres per gm., corresponding to 0.015% adsorbed water. As the vapour pressure isotherm is the same for beaten as for unbeaten cellulose it is probable that the internal surface available for water-bonding is far more important than

the external surface. It is clear, of course, that the above calculations are very empirical, for if every $(C_6H_{10}O_5)$ group bound one water molecule, the water would only amount to 10.5% on the fibre weight. Referring again finally to the paper on the theoretical strength possibilities inherent in the cellulose fibre by H. Mark(136) it is clear that, averaging longitudinal and transverse strengths, it is never possible to utilise the potential fibre bonding capacity to the extent of more than 15 - 20%, and that the figure is probably considerably less for the transverse direction alone. The greater part of such transverse strength is probably inherent in the unbeaten fibre, and is not developed by the beating process.

4. Direct Evidence of Fibre Cohesion after Beating.

The experimental work described in Parts IX and X show that, although the development of strength qualities in the sheet of paper produced from beaten pulp is largely dependent on the final fibre length, yet particularly as regards the bursting and tensile strength there seems to be a fibre cohesion factor which is gradually developed during the beating process. This has been described as due to the formation of a colloidal surface film on the fibres, and has been measured by the extent to which external volume contraction takes place during the free drying of a standard pressed fibre cake. Taking fibre length changes into account, it has been shown to be probable that the other principal strength factor of the beaten sheet is the development of this colloidal surface film, as measured by the cohesion

number of the pulp. Three points can afford to be strongly emphasised, viz., (a) The mechanical action of beating seems to be essential to the development of the cohesion property, a bruising or grinding action being probably more efficient than a direct cutting action. The use of basalt lava rolls in place of sharp bronze knives for beating for strong papers is an instance of this. Beating in another liquid than water can produce the effect, as can dry reduction[58] only provided that there is subsequent immersion in water before cohesion or strength properties are examined. (b) Cohesion and strength properties diminish greatly when the beaten fibre is immersed in a dehydrating or neutral (hydrocarbon) liquid before testing, and this process seems to be quite reversible. (c) Non-cellulose fibres such as asbestos show neither cohesion nor strength properties.

Leaving aside for the moment the actual mechanism of the beating process, it has been shown by W. Lüdtke [142] that artificial fibres and films show the same variation in strength properties when the latter are measured in different liquids, as might be expected from the existence of a hydrated surface film of cellulose acting as an intermediary for the development of fibre-fibre bonding. On the removal of the water film the strength increases, on its restoration the strength diminishes. The phenomena are not quite reversible with paper, but an already formed paper sheet does not lose strength to anything like the same extent by immersion in absolute ethyl alcohol as by immersion in water.

Of course immersion in any liquid whatever will promote fibre slippage to some extent. R.O. Herzog[139] in a recent paper discusses the relation of cellulose to water, alcohol and other liquids. Since the phenomena are specific to water the most natural explanation would appear to be that of a chain of oriented water molecules linking the active hydroxyls of the cohering cellulose micelles, in such a way that the strength of the cohesion would vary as the shortness of the chain. This hypothesis has already been put forward[143], and it would explain the unique position of the water molecule. Ethyl alcohol could not function as a dipole in this sense. Experiments on the effect of wet pressure in sheet making[135] lead to the probable conclusion that the chain of water molecules must be fairly short, if the process is to result in a strong fibre bonding on drying. There must therefore be some obstacle to the formation of such a chain and to the ultimate fibre bonding in the case of unbeaten cellulose. The most natural explanation is the Lüdtke non-cellulosic membrane described in Part III. The beating operation must therefore be necessary to disrupt the membrane at a number of isolated points where cohesion can subsequently take place through the agency of oriented water molecules. The beating may be conducted in the dry state or in the presence of another liquid than water, but the fibre cohesion can only take place in the presence of water. This hypothesis does not mean that water binding cannot take place as far as the unbeaten fibre is concerned. It may well do so, the identity of the

vapour pressure isotherms of beaten and unbeaten cellulose leading one to believe that the hydration does take place in such a case, but there appears to be no experimental means of proving whether such is the case or not. The intact nature of the membrane will prevent cohesion taking place across it, although the membrane may perhaps be permeable to liquid water as well as to water vapour. The latter must certainly be the case.

It is of course possible that the available surface for any form of water bonding is only a very small fraction of the theoretically available micellar surface, but what it is desired to emphasise here is that only a part of this latter surface is made available by the beating process for such water bonding as will eventuate in fibre cohesion in the finished sheet. Even if the water bonding differed in the latter case from the former, it might very well be the case that the difference would not be detectable by a vapour pressure method of investigation. At any rate it has seemed very difficult to the author to explain the fibre cohesion phenomena, without assuming the existence of an inactive surface film on the fibres, which could be disrupted by the beating process. The alcohol dehydration phenomena are again readily explicable on this hypothesis, as no continuous chain of oriented molecules would be possible in such a case. It is not at once easy to see why cohesion should fall away considerably in certain alcohol-water mixtures, but parallel phenomena occur with many lyophilic colloids. W. Pauli[146] points out that the addition of alcohol to aqueous protein sols lowers the

ionisation and dielectric constants of the water and causes the formation of undissociated ions from the preexistent zwitterions. It is clear that there is at least some kind of analogy with the case of cellulose with its coexistent basic and acidic hydroxyl groups, and it may be that one of each sort is necessary to the mechanism of fibre cohesion. The negative results of lyotrope series experiments by the cohesion method is natural enough if the mechanical action of beating really determines the extent of the colloidal surface film. The regularity of the weight-volume drying line is also to be expected, along with the possibility of a curved part near the dry point, where the last water molecules are being eliminated. It is true that the negative results of the experiments on the determination of 'bound' water by the negative adsorption method are somewhat disconcerting. They do not however discredit the present hypothesis, because appreciable values of 'bound' water are at least as probable with an intact as with a ruptured membrane. There is little evidence as yet concerning the permeability of the membrane to different substances.

If surface cohesion were known to develop to a considerable extent in any case without previous rupture of the membrane, the hypothesis would certainly break down completely. This has not been found in any case so far.

It is possible of course that the non-cellulosic membrane is not essential to the explanation of the beating phenomena. In that case we should be practically

forced to accept a partial degradation process of the surface micelles. It would be necessary to assume that the natural cellulose fibres had no free residual valencies available for fibre-fibre bonding in their intact condition, that the beating process disrupted certain of the micelles and developed free residual valencies, and that the development of reducing properties and enhanced copper number in the beaten cellulose would be an accurate measure of the extent of development of the colloidal surface film. The author has not found this to be so, nor has Nakano(56).

Certain serious objections to the 'ruptured membrane' theory of the beating effect must still be stated. The work of the author has been carried out on a bleached sulphite wood pulp of about 84% alpha cellulose content. It is perfectly well known that the beating effect is much more slowly developed on such fibres as cotton, linen and ramie purified by a mild chemical treatment. A pure alpha cellulose pulp also develops the colloidal surface film property very slowly. The individual differences between fibres can be partly explained by considerations of physical micro-structure alone. Again, fibres which have undergone a mercerisation or a partial xanthation treatment are very difficult to beat. Cellulose fibres or films regenerated from the viscose or cuprammonium solvents do not show any spontaneous cohesion property after washing and wet-pressing. The line of demarcation between the α-, β- and γ- celluloses is at best somewhat empirical, and there is not yet available a complete explanation of the varied behaviour

of different celluloses when beaten in presence of water. It would appear to be as well therefore to retain the hypothesis that a partial degradation process of the surface micelles may play a part in the beating phenomena.

It is at least probable that the fibre cohesion due to beating is much less powerful than the transverse micellar bonding within the fibres themselves. A recrystallisation or sintering process may perhaps occur during drying, and may help to explain the lack of complete reversibility of the drying process, but the hypothesis is somewhat uncalled for in the present state of our knowledge.

5. Evidence from Suspension Phenomena.

Most of the results obtained by the method of drainage, electrokinetic potential and surface conductance do not fall into line with those got by the methods of fibre cohesion and strength properties. The drainage results from dehydration by alcohol are an exception. It is unreasonable to assume that dilute solutions of electrolytes can dehydrate the beaten cellulose, and the effect of boiling in water with subsequent cooling is identical. Yet the latter effect has been claimed by Nakano(99) as causing the removal of imbibition water, and by Kanamaru(98) as completing the imbibition process.

A review of the 'measurement of hydration by the boiling method' is given in a recent paper by T. R. Lecompte(147). The boiling method alluded to has already been described in connection with Nakano's experiments. Two measurements are performed with a drainage

tester, the first on the untreated fibre suspension, and the second after boiling in water for an hour and cooling. The loss in 'beating degree' or 'slowness' is taken to be a measure of hydration. Substantially Lecompte agrees with Nakano's conclusions. The same phenomena are described in the paper by Guild and Mills[79] but not so completely, and without the inferences drawn by Nakano. The author must admit that, after observing the ionic coagulation effect on suspensions of beaten fibres, he ceased to attribute any significance, in the sense of hydration or development of colloidal surface film properties to this group of phenomena.

Results obtained by the methods of electrokinetic potential and surface conductance are very difficult to interpret. The diminution of electrokinetic potential in the course of beating may be due to decrease of effective size of particle, as has been shown by Bull and Gortner[93] for quartz, or by dimimution of electric charge. The addition of an electrolyte may reduce the thickness of the double layer and the ζ potential without affecting the charge[97]. The steeping of glass powder in water gradually lowers the ζ potential[91] just as it does with cellulose. Of course it must be admitted that there is a close parallelism between the results obtained by the methods of drainage, rate of evaporation of wet cakes, ζ potential and surface conductance in the case of beaten cellulose. This can be exhibited qualitatively as follows:-

Effect of →	Beatg	Excessive beatg	Steepg.	Boilg. & cooling	Steepg. after boilg. & coolg.
On Drainage	+	+	+	-	- (+ → - Nakano)
On Evaporation	+	-	-		
On ζ Potential	-		- → +	-	+
On Surface conductance	+		+	-	+

+ means slower drainage, greater water content at break in evaporation curve, raised value of ζ or surface conductance.
- means the reverse.

6. Conclusion.

(a) The central phenomenon of beating, apart from fibre reduction, is the formation over a part of the fibre surface of a colloidal film, which is the cause of the subsequent fibre-fibre bonding in the sheet.

(b) The best practical measure of this effect is the free volume contraction of a standard pressed fibre cake on drying in a standard manner. Correction of the result for fibre reduction and air elimination is obtainable by comparison with a similar cake previously dehydrated in alcohol.

(c) Mechanical abrasion or rupture of the fibre is an essential feature of the beating process, as the colloidal surface film is probably only developed where the Lüdtke membrane system has been destroyed. The most durable papers will be obtained where the colloidal surface film has been developed with the least possible damage to the fibres, and where the surface film development does not unduly sacrifice the property of elasticity to that of strength.

(d) The colloidal surface film does not develop in any other liquid than water, but fibre felting as well

as beating can take place in other liquids. If beating takes place in alcohol, for instance, the colloidal surface film is developed extremely rapidly whenever the fibres are immersed in water. The mechanical effects of beating in non-aqueous liquids are quite different from those obtained by beating in water. The fibres are more brittle and less soft, and tend to break across rather than to split lengthwise. Hence the maximum strength development cannot take place. (See microphotograph (2) page 208B)

(e) It is difficult to explain the beating phenomena of pure alpha cellulose and of mercerised or partly xanthated and subsequently reverted fibres without the hypothesis that the surface micelles are partially degraded in some way.

(f) Drainage tests have only an indirect connection with the cohesion potentialities of the beaten fibre. Suspensions of beaten cellulose fibres behave in an analogous manner to electro-negative suspensoids, and are very sensitive to small concentrations of electrolytes. They also exhibit dehydration phenomena in the presence of alcohol and glycerol water mixtures.

References XI.

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